# *TRANSACTIONS*

*American Society for Metals*

VOL. XXXII 1944


## TECHNICAL PROGRAM AND REPORTS OF OFFICERS AMERICAN SOCIETY FOR METALS—25th ANNUAL CONVENTION, CHICAGO, OCTOBER 18 to 22, 1943

FOR the benefit of members who were not in attendance at the Twenty-fifth Annual Convention of the Society, held in Chicago, October 18 to 22, 1943, and for purposes of record, the Technical Papers Program, the Production, Conservation and Post-War Planning Group Meetings, and Reports of Officers presented at the annual meeting are herewith published in full.

### TECHNICAL PAPERS PROGRAM

### MONDAY, OCTOBER 18

**Ballroom, Palmer House—9:30 A. M.**

*Session on Quenching and Hardenability*

Joint Chairmen—M. A. Grossmann and Howard Scott

*Quenching and Hardenability of Hollow Cylinders,* by J. H. Hollomon and C. Zener, Watertown Arsenal.

*Rates of Cooling in Blocks and Cylinders,* by C. B. Post and W. H. Fenstermacher, Carpenter Steel Co.

*An Evaluation of Quenching Oils,* by E. K. Spring, P. T. Lansdale and C. W. Alexander, Henry Disston & Sons, Inc.

**Room No. 14, Palmer House—9:30 A. M.**

*Research Session*

Joint Chairmen—E. G. Mahin and A. R. Troiano

*Dimensional Changes Encountered in Tube Sinking,* by W. M. Baldwin, Jr. and T. S. Howald, Chase Brass & Copper Co.

*A Metallographic Study of the Decomposition of Austenite in Manganese Steels,* by John V. Russell, Republic Steel Corp., and Francis T. McGuire, University of Kentucky.

**Red Lacquer Room, Palmer House—9:30 A. M.**

*Session on Crystalline Structure*

Joint Chairmen—C. S. Barrett and B. F. Shepherd

*The Microhardness Tester as a Metallurgical Tool,* by Constance B. Brodie, General Electric Co.

*Intercrystalline Cohesion of Metals,* by E. R. Parker, General Electric Co.

*Plastic Flow and Rupture of Metals,* by C. Zener and J. H. Hollomon, Watertown Arsenal.

**Ballroom, Palmer House—11:30 A. M.**
*Victory Session—Labor*
Speaker: W. H. Wheatro, chief of office of Labor Production, Region 6.

**Ballroom, Palmer House—2:00 P. M.**
*Group Meeting on Advanced Quenching Practice*

**Red Lacquer Room, Palmer House—2:00 P. M.**
*Group Meeting on Boron in Steel and Iron*

**Ballroom, Palmer House—8:30 P. M.**
*Group Meeting on Purchase of Steels on Performance Rather Than Analysis*

**Red Lacquer Room, Palmer House—8:30 P. M.**
*Group Meeting on Non-Destructive Tests*

## TUESDAY, OCTOBER 19

**Ballroom, Palmer House—9:30 A. M.**
*Session on Transformation of Austenite*
Joint Chairmen—E. G. Mahin and Gilbert Soler

*The Effect of Varying Amounts of Martensite Upon the Isothermal Transformation of Austenite Remaining After Controlled Quenching,* by H. J. Elmendorf, American Steel & Wire Co.

*Martensite Reactions in Alloy Steels,* by Peter Payson and Charles H. Savage, Crucible Steel Company of America.

*Influence of Nickel, Molybdenum, Cobalt and Silicon on the Kinetics and Ar" Temperatures of the Austenite to Martensite Transformation in Steels,* by H. H. Chiswik, Battelle Memorial Institute, and A. B. Greninger, University of Chicago.

**Red Lacquer Room, Palmer House—9:30 A. M.**
*Physical Properties Session*
Joint Chairmen—H. A. Anderson and J. J. Kanter

*High Speed Testing of Mild Steel,* by J. H. Hollomon and C. Zener, Watertown Arsenal.

*The Effect of Heat Treatment and Carbon Content on the Work Hardening Characteristics of Several Steels,* by John H. Hollomon, Watertown Arsenal.

*The Tensile Properties of Alloyed Ferrites,* by C. E. Lacy, International Nickel Co., and M. Gensamer, Carnegie Institute of Technology.

**Room No. 14, Palmer House—9:30 A. M.**
*Case Hardening Session*
Joint Chairmen—H. B. Knowlton and Clair Upthegrove

*A Study of the Nitriding Process—I. Effect of Ammonia Dissociation on Case Depth and Structure,* by Carl F. Floe, The Nitralloy Corp.

*The Action of Carbonate Catalysts in the Carburization of Steel,* by T. C. Fong and R. A. Ragatz, University of Wisconsin.

*The Isothermal Transformation of Case-Carburized S.A.E. 4815,* by J. R. Cruciger and J. R. Vilella, United States Steel Corp.

**Ballroom, Palmer House—11:30 A. M.**
*Victory Session—Business*

*Post-War Planning,* by Bennett Chapple, assistant to President, American Rolling Mill Co.

**Red Lacquer Room, Palmer House—2:00 P. M.**
*Group Meeting on Powder Metals*

**Ballroom, Palmer House—2:00 P. M.**
*Group Meeting on Steels with Intensifiers*

**Room No. 14, Palmer House—4:00 P. M.**
*Group Meeting on Foundry Metallurgy*

**Ballroom, Palmer House—8:30 P. M.**
*Group Meeting on Steel Making Methods*

## WEDNESDAY, OCTOBER 20

**Ballroom, Palmer House—9:30 A. M.**
*Annual Meeting of the American Society for Metals*
*Edward de Mille Campbell Memorial Lecture,*
by Dr. C. H. Mathewson, Chairman of the Department of Metallurgy, Yale University
H. J. French, Chairman

**Ballroom, Palmer House—2:00 P. M.**
*Group Meeting on Post-War Planning in Non-Ferrous Metals*

**Red Lacquer Room, Palmer House—2:00 P. M.**
*Group Meeting on Modern Practice in Surface Hardening*

**Room No. 14, Palmer House—4:00 P. M.**
*Group Meeting on Consumer Control of Quality by Inspection*

**Ballroom, Palmer House—8:30 P. M.**
*Group Meeting on National Emergency Steels*

## THURSDAY, OCTOBER 21

**Room No. 14, Palmer House—9:30 A. M.**
*Precipitation Hardening Session*
Joint Chairmen—E. C. Bain and K. R. Van Horn

*Order Hardening: Its Mechanism and Recognition,* by David Harker, General Electric Co.

*Interrupted Quench and Isothermal Treatments of Precipitation Hardening Alloys: Introductory Notes,* by R. H. Harrington, General Electric Co.

**Red Lacquer Room, Palmer House—9:30 A. M.**
*Heat Treatment Session*
Joint Chairmen—S. L. Hoyt and W. E. Jominy

*Bright Gas Quenching of S.A.E. X-4130 Welded Aircraft Tubes,* by Wm. Lehrer, Surface Combustion.

*Some Effects of Heat Treatment on Low Alloy Titanium Steels,* by George F. Comstock, Titanium Alloy Manufacturing Co.

*Effect of Time, Temperature and Prior Structure on the Hardenability of Several Alloy Steels,* by J. Welchner, E. S. Rowland and J. E. Ubben, Timken Roller Bearing Co.

**Ballroom, Palmer House—9:30 A. M.**
*Physical Properties Session*
Joint Chairmen—A. E. Focke and C. W. MacGregor

*The Stress Distribution at the Neck of a Tension Specimen,* by P. W. Bridgman, Harvard University.

*Notched Bar Tensile Test Characteristics of Heat Treated Low Alloy Steels,* by G. Sachs, J. D. Lubahn and L. J. Ebert, Case School of Applied Science.

*The Strength of Heat Treated Alloy Steel Bolts,* by G. Sachs, P. S. Cole and R. A. Roth, Case School of Applied Science

**Ballroom, Palmer House—11:30 A. M.**
*Victory Session—Army*
Speaker—Brig. Gen. Herman F. Safford, Chief of Production Service Branch, Office of the Chief of Ordnance.

**Ballroom, Palmer House—2:00 P. M.**
*Group Meeting on Fundamental Changes in Metallurgy and Metals*

**Red Lacquer Room, Palmer House—2:00 P. M.**
*Group Meeting on Light Weight Construction*

**Room No. 14, Palmer House—4:00 P. M.**
*Group Meeting on Salvage*

**Ballroom, Palmer House—7:00 P. M.**
*Annual Dinner of the American Society for Metals*

## FRIDAY, OCTOBER 22

**Room No. 14, Palmer House—9:30 A. M.**
*Metallography Session*
Joint Chairmen—T. G. Digges and S. P. Watkins

*The Emissivity of Molten Stainless Steels,* by George N. Goller, Rustless Iron and Steel Corp.

*Quenching Rate Versus Graphite Formation in Prequenched White Cast Iron,* by Orien W. Simmons, Battelle Memorial Institute.

*Pseudomorphs of Pearlite in Quenched Steel,* by Owen W. Ellis, Ontario Research Foundation.

**Ballroom, Palmer House—9:30 A. M.**
*Session on Tempering of Steel*
Joint Chairmen—J. P. Gill and F. N. Rhines

*Structural Changes During the Tempering of High Carbon Steel,* by D. P. Antia, S. G. Fletcher and Morris Cohen, Massachusetts Institute of Technology.

*The Effect of Carbon on the Tempering of Steel,* by Stewart G. Fletcher and Morris Cohen, Massachusetts Institute of Technology.

*The Tempering of Nickel and Nickel-Molybdenum Steels,* by Dara P. Antia and Morris Cohen, Massachusetts Institute of Technology.

*Effect of Quenching-Bath Temperature on the Tempering of High Speed Steel,* by Paul Gordon and M. Cohen, Massachusetts Institute of Technology, and R. S. Rose, Vanadium-Alloys Steel Co.

**Red Lacquer Room, Palmer House—9:30 A. M.**
*Session on High Temperature Properties*
Joint Chairmen—H. L. Maxwell and E. R. Parker

*An Emergency Heat Resistant Alloy,* by O. E. Harder and James T. Gow, Battelle Memorial Institute.

*An Optimum Silicon Range in Plain and 2.0 Per Cent Chromium Cast Irons Exposed to Elevated Temperatures, by* C. O. Burgess and R. W. Bishop, Union Carbide & Carbon Research Laboratories.

*Creep Strength, Stability of Microstructure and Oxidation Resistance of Chromium-Molybdenum and Chromium-Nickel Steels,* by R. F. Miller, W. G. Benz and M. J. Day, United States Steel Corp.

**Ballroom, Palmer House—11:30 A. M.**
*Victory Session—Navy*
Speaker—Capt. G. D. Linke, U.S.N., Chief of Armor Projectile and Bomb Section, Bureau of Ordnance.

**Ballroom, Palmer House—2:00 P. M.**
*Group Meeting on Magnesium and Magnesium Alloys*

**Red Lacquer Room, Palmer House—2:00 P. M.**
*Group Meeting on Special Finishes and Metallic Protection*

**A.S.M. Group Meetings on Production, Conservation, and Post-War Planning**

*In order to concentrate on production, conservation, and post-war planning—the general theme of National Metal Congress and War Conference Displays—all A.S.M. Technical Sessions were held in the mornings, leaving afternoons and evenings open for group discussion meetings. These meetings were patterned after the successful forums of the past two years. A panel of experts sat before microphones; each in turn gave a 10-minute off-the-record discussion of his specialty, and then answered questions from the audience. Finally the summarizer emphasized the important points that had arisen.*

## MONDAY, OCTOBER 18

**Ballroom, Palmer House—2:00 P. M.**
*Advanced Quenching Practice*
Chairman—Harry W. McQuaid, Assistant Chief Metallurgist, Republic Steel Corp.
Summarizer—Herbert J. French, Assistant Manager, Development and Research Division, International Nickel Co.

*A—Complete Quench*

*Oils and Oil Quenching,* by Blaine B. Wescott, Chief Metallurgist, Gulf Research & Development Corp.
*Spray-Oil Quench and Quenching Fixtures for Violent Turbulence,* by Roy H. Weber, Supt. of Heat Treating, Cadillac Motor Car Div., General Motors Corp.
*Bright Gas Quenching,* by Armand Di Giulio, Head Research Div., Bundy Tubing Co.
*Super-Cooling,* by S. F. Urban, Carnegie-Illinois Steel Corp.
*General Discussion by the Audience.*

*B—Incomplete Quench*

*Hot Quenching (Austempering),* by Harold J. Elmendorf, Research Engineer, American Steel and Wire Co.
*Timed Quenching,* by Muir L. Frey, Aircraft Met., Packard Motor Car Co.
*Martempering,* by B. F. Shepherd, Chief Metallurgist, Ingersoll-Rand Co.
*General Discussion by the Audience.*

*C—Summary of Important Points*

**Red Lacquer Room, Palmer House—2:00 P. M.**
*Boron in Steel and Iron (Sampling and Analysis)*
Chairman—Norman F. Tisdale, Metallurgist, Molybdenum Corp. of America.
Summarizer—George R. Fitterer, Head Department of Metallurgical Engineering, University of Pittsburgh

*Methods for Sampling (a) Liquid Steel, (b) Bar Stock,* by George T. Motok, Director, Research and Development Division, Republic Steel Corp.
*Boron by the Quinalizarin Method,* by L. C. Flickinger, Youngstown Sheet & Tube Co.
*Boron by Colorimetric Determinations,* by Richard W. Lewis, Asst. Chief Chemist, Jones & Laughlin Steel Corp.
*Distillation-Titration Methods,* by John L. Hague, Bureau of Standards.

*Spectrographic Technique Especially Adaptable for Boron Determinations,* by P. R. Irish, Research Engineer, Development and Research Department, Bethlehem Steel Co.

*Experiences in Boron Determinations by the Spectrograph,* by J. Alfred Berger, Molybdenum Corp. of America.

*General Discussion by the Audience.*

*Summary of Important Points*

**Ballroom, Palmer House—8:30 P. M.**

*Purchase of Steels on Performance Rather Than Analysis*

Chairman—Col. H. H. Zornig, Officer in Charge, Research Laboratory, Watertown Arsenal

Summarizer—Jerome J. Kanter, Materials Research Engineer, Crane Co.

*A—Statement of the Commercial Problem*

*Continental System of Specification on Properties,* by Ernest E. Thum, Editor, METAL PROGRESS.

*American System of Specification by Analysis,* by Earle C. Smith, Chief Metallurgist, Republic Steel Corp.

*Acceptance on Performance Tests,* by G. C. Riegel, Chief Metallurgist, Caterpillar Tractor Co.

*General Discussion by the Audience.*

*B—Technical Aspects*

*Interchangeability of Heat Treated Steels,* by Walter G. Patton, Satistician, Climax Molybdenum Co.

*Hardenability Test, Its Limitations in Appraising Alternate Steels, and Proper Method of Specification,* by Walter E. Jominy, Dodge Chicago Plant, Chrysler Corp.

*Correlation of Laboratory Tests to Performance in Service,* by J. O. Almen, General Motors Research Laboratories.

*Problems Applying Especially to Tool Steels,* by S. C. Spalding, Metallurgical Engineer, American Brass Co.

*General Discussion by the Audience.*

*C—Summary of Important Points*

**Red Lacquer Room, Palmer House—8:30 P. M.**

*Non-Destructive Tests*

Chairman—A. V. de Forest, Professor of Mechanical Engineering, Massachusetts Institute of Technology

Summarizer—V. N. Krivobok, Chief Metallurgist, Lockheed Aircraft Corp.

*A—Surface Appraisal*

*Inspection of Rough Materials,* by M. D. Johnson, Chief Inspector, Caterpillar Tractor Co.

*Appraisal of Surface Finishes,* by Mary R. Norton, Associate Metallurgist, Watertown Arsenal.

*Strain-Gages, Stress Markers, Etc.,* by F. C. Tatnall, Manager, Testing Equipment Department, Baldwin Southwark Division.

*General Discussion by the Audience.*

*B—Sub-Surface Inspection*

*Interpretation of Magnaflux (and Allied Methods),* by R. W. Anderson, Metallurgist, Allison Div., General Motors Corp.

*Laminations in Sheet,* by H. S. Van Vleet, Metallurgical Engineer, American Can Co.

*Continuity Testing by Electron Devices,* by P. E. Cavanagh, Metallurgist, Allen B. Du Mont Laboratories, Inc.

*X-Ray Inspection,* by Kent R. Van Horn, Research Metallurgist, Aluminum Co. of America.

*General Discussion by the Audience.*

*C—Summary of Important Points*

## TUESDAY, OCTOBER 19

**Red Lacquer Room, Palmer House—2:00 P. M.**

*Powder Metals*

Chairman—P. M. McKenna, President, Kennametal, Inc.
Summarizer—N. P. Koehring, Metallurgist, Moraine Products Div., General Motors Corp.

*A—Wartime Developments*

*Economical Raw Materials and Manufacture of Powders,* by H. E. Hall, General Manager, Metals Disintegrating Co.

*Compacts Useful for Unique Physical Properties,* by E. I. Larsen, Metallurgical Engineer, P. R. Mallory & Co.

*Metal Sponges (Articles with Controlled Porosity),* by Carl Claus, Research Engineer, Bound Brook Oilless Bearing Co.

*General Discussion by the Audience.*

*B—Post-War Possibilities*

*Limitations as to Size and Shape,* by Walter C. Sutton, Chief Engineer, S. K. Wellman Co.

*Industrial Metal Powder Research Directed Toward Post-War Application,* by J. F. Kusmick, Asst. Div. Research, Stevens Institute of Technology.

*General Discussion by the Audience.*

*C—Summary of Important Points*

**Ballroom, Palmer House—2:00 P. M.**

*Steels With Intensifiers (Special Alloy Addition Agents)*

Chairman—H. B. Knowlton, International Harvester Co.
Summarizer—L. E. Ekholm, Metallurgical Engineer, Alan Wood Steel Co.

*A—Production Aspects*

*Difference in the Available Agents—Nature, Use, Effects (Steel Making End),* by T. W. Merrill, Metallurgist, Vanadium Corp. of America.

*Intensifiers in Castings,* by Fred T. C. Daniels, Vice-President, Mackintosh-Hemphill Co.

*Commercial Availability of the Wrought Steels,* by Clarence Altenberger, Research Engineer, Great Lakes Steel Corp.

*General Discussion by the Audience.*

*B—Consumers' Problems*

*How to Specify Intensified Steels,* by N. F. Tisdale, Metallurgist, Molybdenum Corp. of America.

*How to Inspect and Check Deliveries,* by A. E. Focke, Chief Met., Diamond Chain & Mfg. Co.

*Experience with Intensified Steels in Production,* by Vernon E. Hense, Assistant Chief Metallurgist, Buick Motor Division, General Motors Corp.

*General Discussion by the Audience.*

*C—Summary of Important Points*

**Room No. 14, Palmer House—4:00 P. M.**

*Foundry Metallurgy (Improved Castings)*

Chairman—Karl F. Schmidt, Metallurgist, United Engineering & Foundry Co.
Summarizer—V. A. Crosby, Climax Molybdenum Co.

*A—Iron and Steel Founding*

*Advanced Melting Methods,* by G. A. Lilleqvist, Research Director, American Steel Foundries.

*High Strength Cast Irons,* by G. L. Richter, Metallurgist, Farrel-Birmingham Co.

*High Ductility, High Strength Cast Steels,* by Carl F. Joseph, Chief Metallurgist, Saginaw Malleable Iron Div., General Motors Corp.

*Centrifugal Casting,* by C. K. Donoho, Metallurgist, American Cast Iron Pipe Co.

*General Discussion by the Audience.*

*B—Non-Ferrous Founding*

*Continuous Casting of Ingots or Shapes,* by Albert J. Phillips, Superintendent of Research, American Smelting & Refining Co.

*Pressure Molded Die Castings,* by D. Basch, Works Laboratory, General Electric Co.

*General Discussion by the Audience.*

*C—Summary of Important Points*

**Ballroom, Palmer House—8:30 P. M.**

*Steel Making Methods—More and Better Steels*

Chairman—H. W. Graham, Director of Metallurgy and Research, Jones & Laughlin Steel Corp.

Summarizer—J. Hunter Nead, Chief Metallurgist, Inland Steel Co.

*A—More and Better Openhearth Steel*

*Improving Efficiency in Openhearth Plants,* by William C. Buell, Jr., Steel Plant Consultant, Arthur G. McKee & Co.

*Basic Openhearth as a Producer of Fine and Alloy Steels,* by C. D. King, United States Steel Corp.

*Acid Openhearth as a Producer of Fine and Alloy Steels,* by F. B. Foley, Superintendent of Research, The Midvale Co.

*General Discussion by the Audience.*

*B—Post-War Planning in Electric Steel*

*Hot Metal to Electric Furnaces,* by Earle C. Smith, Chief Metallurgist, Republic Steel Corp.

*Quality Considerations, Openhearth Versus Electric Steel,* by Gilbert Soler, Manager of Research and Mill Metallurgy, Timken Roller Bearing Co.

*General Discussion by the Audience.*

*C—Summary of Important Points*

## WEDNESDAY, OCTOBER 20

**Ballroom, Palmer House—2:00 P. M.**

*Post-War Planning in Non-Ferrous Metals (Supply and Demand)*

Chairman—Zay Jeffries, Technical Director, Lamp Department, General Electric Co.

Summarizer—Col. A. E. White, Department of Engineering Research, University of Michigan.

*Where Are We Going to Use All the Aluminum We Can Easily Make?* by Safford K. Colby, Vice-President, Aluminum Co. of America.

*Probable Competitive Position of Magnesium and Its Alloys,* by L. B. Grant, Sales Manager, Magnesium Div., Dow Chemical Co.

*Zinc, Zinc Coatings and Zinc Alloys,* by Ernest V. Gent, Secretary, American Zinc Institute.

*Lead, the Only Common Metal Relatively Plentiful,* by F. E. Wormser, Secretary, Lead Industries Association.

*Stockpiles to Absorb Stocks in Process and to Correct Trade Balances,* by F. W. Willard, President, Nassau Smelting and Refining Co.

*General Discussion by the Audience.*

*Summary of Important Points*

**Red Lacquer Room, Palmer House—2:00 P. M.**

*Modern Practice in Surface Hardening*

Chairman—Roy W. Roush, Chief Metallurgist, Timken-Detroit Axle Co.

Summarizer—Marcus A. Grossmann, Director of Research, Carnegie-Illinois Steel Corp.

*A—Gas Carburizing*

*Controlled Gas Carburizing and Diffusion Cycles,* by F. E. Harris, Furnace Engineer, Buick Motor Div., General Motors Corp.

*So-Called "Graphite" in Carburized Cases,* by John Welchner, Metallurgical Dept., Timken Steel & Tube Div.

*General Discussion by the Audience.*

*B—Hard Layers on Tool Steels*

*Hard Layers (Carburizing; Chrome Plating) on Tool Steels,* by J. P. Gill, Chief Metallurgist, Vanadium-Alloys Steel Co.

*General Discussion by the Audience.*

*C—Differential Hardening*

*By High Frequency Current,* by F. F. Vaughn, Asst. Chief Metallurgist, Caterpillar Tractor Co.

*By Gas Flame,* by Gordon T. Williams, Metallurgist, Deere & Co.

*Utility of Jominy Hardenability Test for Steels for Surface Hardening,* by O. W. McMullan Metallurgist, Youngstown Sheet & Tube Co.

*General Discussion by the Audience.*

*D—Summary of Important Points*

**Room No. 14, Palmer House—4:00 P. M.**

*Quality Control (Consumer Control of Quality by Inspection)*

Chairman—A. C. Richmond, Chief, Inspection Division, Chicago Ordnance District

Summarzier—J. W. Dunn, Director of Quality, Curtiss-Wright Corp., Airplane Division

*A—Having to Do With the Personal Equation*

*Separating Important from Unimportant Inspection Operations,* by A. W. F. Green, Materials Engineer, Pratt & Whitney Aircraft Corp. of Mo.

*The Personal Equation in Inspection,* by John W. W. Sullivan, Industrial Division, Cleveland Ordnance District.

*Acceptance Control—Not "How Much" Inspection, but "How Good",* by L. E. Ekholm, Metallurgical Engineer, Alan Wood Steel Co.

*General Discussion by the Audience.*

*B—Having to Do With the Process*

*Precision Measurments,* by John A. Harrington, President, Savage Tool Co.

*Maintenance of Uniformity, Heat to Heat,* by A. N. Swanson, Chief Metallurgist, Gary Works, Carnegie-Illinois Steel Corp.

*Statistical Analysis of Test Results,* by Charles S. Gotwals, SKF Industries, Inc.

*General Discussion by the Audience.*

*C—Specific Application*

*Specific Application to Ammunition Manufacture,* by H. R. Bellinson, Ammunition Branch, Office of Chief of Ordnance.

*General Discussion by the Audience.*

*D—Summary of Important Points*

**Ballroom, Palmer House—8:30 P. M.**

*National Emergency Steels*

Chairman—H. LeRoy Whitney, Technical Consultant to the Chairman, W.P.B.

Summarizer—Glen C. Riegel, Chief Metallurgist, Caterpillar Tractor Co.

*A—War Developments*

*Review of Cooperative Developments,* by Lt. Col. John Frye, Office of the Chief of Ordnance.

*Present Utility, Production and Use of NE Steels,* by Charles Parker, Secretary, General Technical Committee, American Iron and Steel Institute.

*Use of NE Steels in Aircraft and Engines,* by J. B. Johnson, Chief, Materials Laboratory, Army Air Forces, Wright Field.

*General Discussion by the Audience.*

*B—Post-War Planning*

*Present and Prospective Supplies of Alloying Elements,* by Francis B. Foley, Superintendent of Research, The Midvale Co.

*Future Trend in Mild and Medium Alloy Steel Developments,* by D. H. Ruhnke, Metallurgical Engineer, Central Alloy District, Republic Steel Corp.

*Future Trend in High Alloy Steel Developments,* by S. M. Norwood, Electro Metallurgical Co.
*General Discussion by the Audience.*

*C—Summary of Important Points*

## THURSDAY, OCTOBER 21

**Ballroom, Palmer House—2:00 P. M.**

*Fundamental Changes Reasonably Expected in Metallurgy and Metals (Post-War Planning)*

Chairman—Robert F. Mehl, Head, Department of Metallurgy, Carnegie Institue of Technology
Summarizer—John H. Van Deventer, Editor, *The Iron Age*

*A—Melting and Refining*

*Iron and Steel Melting and Refining Methods,* by Harold Emerick, Steel Works Metallurgist, Jones & Laughlin Steel Corp.
*Light Metal Reduction Processes,* by R. L. Sebastian, Magnesium Branch WPB.
*Non-Ferrous Metals,* by A. J. Phillips, Superintendent of Research, American Smelting & Refining Co.
*General Discussion by the Audience.*

*B—Fabrication and Treatment*

*Future Heat Treating Methods,* by R. J. Cowan, Surface Combustion.
*Fabrication Methods (Casting, Forging, Machining, Welding),* by Eric Oberg, Editor, *Machinery.*
*Improved Finishes (Clad, Plating, Plastics, Paint),* by Harry P. Coats, Chief Chemist and Metallurgist, Firestone Steel Products Co.
*General Discussion by the Audience.*

*C—Summary of Important Points*

**Red Lacquer Room, Palmer House—2:00 P. M.**

*Light Weight Construction for the Post-War Era*

Chairman—E. E. Thum, Editor of METAL PROGRESS
Summarizer—Edgar C. Bain, Vice-President, Carnegie-Illinois Steel Corp.

*A—Light Metals*

*Aluminum for Favorable Strength-Weight Ratio,* by V. N. Krivobok, Chief Metallurgist, Lockheed Aircraft Co.
*Magnesium as an Engineering Metal,* by V. N. Krivobok, Chief Metallurgist, Lockheed Aircraft Co.
*General Discussion by the Audience.*

*B—Steels*

*Stainless Steel for Structural Purposes,* by Russell Franks, Union Carbide & Carbon Research Laboratories.
*High Strength, Mild Alloy Steel, Used as Rolled,* by E. H. Davidson, Metallurgical Engineer, Carnegie-Illinois Steel Corp.
*General Discussion by the Audience.*

*C—Non-Metallics*

*Plastics; Nature and Quantity Now Available Which Are Good Enough to Compete With Metal,* by William A. Safka, Glenn L. Martin Co.
*General Discussion by the Audience.*

*D—Summary of Important Points*

**Room No. 14, Palmer House—4:00 P. M.**

*Salvage*

Chairman—H. A. Anderson, Western Electric Co.
Summarizer—Burns George, Metallurgical Engineer, Vanadium-Alloys Steel Co.

*A—Salvaging the Metal*

*Need for Segregating Scrap at the Source,* by Robert A. Wheeler, Manager of Publicity, International Nickel Co.
*Maintaining the Identity of Metals and Scrap,* by R. C. Banks, Wilcox-Rich Div., Eaton Mfg. Co.

*Recovery of Battlefield Scrap,* by Lt. Col. Charles L. Austin, Chief Redistribution and Salvage Branch, Production Div., Hq., A.S.F.
*General Discussion by the Audience.*

*B—Getting the Metal Back Into Use*

*Use of Aluminum Scrap,* by Walter Bonsack, National Smelting Co.
*Use of Brass Cartridge Scrap,* by H. A. Anderson, Engineer, Metallic Raw Materials, Western Electric Co.
*Saving and Disposal of Tool Steel Scrap,* by John D. Sullivan, Battelle Memorial Institute
*General Discussion by the Audience.*
*International Harvester's Clinic on Tool Salvage.*

*C—Summary of Important Points*

## FRIDAY, OCTOBER 22

**Ballroom, Palmer House—2:00 P. M.**

*Magnesium and Magnesium Alloys*

Chairman—John A. Gann, Dow Chemical Co.
Summarizer—W. H. Finkelday, Singmaster & Breyer

*A—Castings*

*Special Precautions in the Foundry and Heat Treatment and Impregnation,* by C. E. Nelson, Metallurgist, Dow Chemical Co.
*Die Castings,* by Joseph C. Fox, Doehler Die Casting Co.
*General Discussion by the Audience.*

*B—Fabrication*

*Pressing and Forming of Sheet,* by J. V. Winkler, Development Engineer, Dow Chemical Co.
*Machining, Cutting Tools and Precautions,* by Arthur A. Schwartz, Chief Tool Research Engineer, Bell Aircraft Corp.
*Welding of Magnesium and Magnesium Alloys by the Helium Shielded Arc Method,* by Frank A. Wassell, Welding Engineer, General Electric Co.
*General Discussion by the Audience.*
*Dow Chemical Company's Film on "The Working of Magnesium Alloys"*

*C—Summary of Important Points*

**Red Lacquer Room, Palmer House—2:00 P. M.**

*Special Finishes and Metallic Protection*

Chairman—J. L. McCloud, Metallurgical and Chemical Engineering Dept., Ford Motor Co.
Summarizer—Harry P. Coats, Chief Chemist and Metallurgist, Firestone Steel Products Co.

*A—Prior Considerations*

*Cleaning Prior to Finishing,* by J. R. Ewing, Assistant to President, Solventol Chemical Products, Inc.
*Slushing Compounds,* by Fred E. Stockwell, Industrial Lubrication Engineer, Colonial Beacon Oil Co.
*General Discussion by the Audience.*

*B—Electroplates*

*Electrotinning,* by Bruce Gonser, Battelle Memorial Institute.
*General Discussion by the Audience.*

*C—Chemical Coatings*

*Chemical Coatings on Steel,* by V. M. Darsey, Technical Director, Parker Rust-Proof Co.
*Chemical Coatings on Aluminum,* by Ralph E. Pettit, Aluminum Research Laboratories.
*Chemical Coatings on Magnesium,* by W. S. Loose, Dow Chemical Co.
*Plastic Coatings (Protecting the Steel Cartridge Case),* by Lt. Col. H. R. Turner, Cartridge Case Industry Committee.
*General Discussion by the Audience.*

*D—Summary of Important Points*

# ANNUAL ADDRESS OF THE PRESIDENT

HERBERT J. FRENCH, *President*

*Twenty-fifth Annual Convention, Chicago, October 20, 1943*

MEMBERS of the American Society for Metals may feel gratified by the record of progress of the Society during the past twelve months. Now composed of over 17,000 members from practically all branches of the metals industries, the Society represents a virile force in the industrial part of the Nation's war effort. Many members are directly connected with war production, while others have found opportunity to serve on War Industry Committees. In addition, there are those who have assumed essential roles in military activities or in the civilian government.

The Society has maintained its service to members in this wartime period and has had a satisfactory financial year, as will be described in detail in the reports of your Secretary and Treasurer.

## *New Chapters*

Outstanding among developments has been the formation of seven new Chapters, all of which embarked on careers of service during the past twelve months. These new Chapters are—San Diego and Spokane in the Pacific Coast area; Wichita, Kansas, and Warren, Ohio, in the Central West; Georgia and Louisville in the South; and Manitoba in Canada. They bring the total of the Chapters in the Society to an all-time peak of 62.

## *New Awards*

Attention should be called to two new awards created by the Board of Trustees for achievements in the metals industries.

The first of these is known as "The Gold Medal of the American Society for Metals", and is to be awarded to a candidate "who, having attained the age of fifty and having become recognized for his outstanding metallurgical knowledge. shall have shown great versatility in the application of science to the metal industry."

The second of the new awards is known as "The A.S.M. Medal for the Advancement of Research". It is to be awarded to a candidate who is "an executive in an industrial organization, the principal activity of which is the production or fabrication of metals. He shall be one who, over a period of years, has consistently sponsored metal-

lurgical research or development and by his foresight and his influence in making available financial support has helped substantially to advance the arts and sciences relating to metals."

The stated objectives of both of these awards reflect those upon which the Society itself was founded, and the initial presentations will be made at the Annual Dinner, Thursday, October 21, 1943.

### *Board Meetings*

The Board of Trustees held four meetings during the year—October 30, 1942; May 7, 1943; August 27, 1943, and October 19, 1943.

### *Medals*

The President's Medal was presented to Dr. O. E. Harder at the Annual Dinner held in Cleveland, October 15, 1942.

The Henry Marion Howe Medal was awarded at the Annual Dinner in Cleveland, October 15, 1942, to W. A. Schlegel, Metallurgical Department, Carpenter Steel Company, Reading, Pennsylvania, for his paper entitled "Surface Carbon Chemistry and Grain Size of 18-4-1 High Speed Steel." This paper was presented to the Society at the Cleveland Convention in 1940, and was published in the September 1941 issue of TRANSACTIONS.

The Campbell Memorial Lecture (established in 1925) was presented in 1942 by John Chipman, professor of metallurgy, Massachusetts Institute of Technology, Cambridge, Massachusetts, on the subject "Chemistry at 1600" and was published in TRANSACTIONS for December 1942.

The Sauveur Achievement Award, established in 1934, was presented at the Annual Dinner in 1942 to Benjamin F. Shepherd, Past President of the A.S.M., and Chief Metallurgist, Ingersoll-Rand Company, Phillipsburg, New Jersey, for his contribution to metallurgical knowledge through his pioneering work on the hardenability of high carbon tool steels.

### *Chapter Visits*

During the twelve months ending October 1943 your President visited thirty-two Chapters of the Society. These visits, which included conferences with executive committees, nearly all were made with your National Secretary and required travel of over 20,000 miles from Canada on the north to the Gulf Coast on the south; and

from Boston, New York and Baltimore in the east to California, Oregon and Washington in the west. Included was one Regional Meeting in which several additional Chapters took part. Without exception, Chapter organizations were found to be alert and active, especially in war work. The handling of local problems was very generally supplemented by keen interest in the affairs of other Chapters and the welfare of the Society as a whole. This has been evident over a period of time by the many suggestions coming directly to National Headquarters or through the Officers of the Society or Members of the Board.

### *Standing Committees*

The several standing committees of the Society functioned effectively and efficiently throughout the year. These comprise committees on the METALS HANDBOOK; METAL PROGRESS; Finance; Publication; Education; Constitution and By-Laws. Certain of the activities of these groups are mentioned in detail later in this report, but special thanks are due the members of the Finance Committee for their studies and careful appraisals of the Society's financial problems and their recommendations to the Board intended to conserve the capital assets of the Society in this uncertain war-time period.

### *Publications*

METAL PROGRESS remains the vehicle by which timely, informative articles reach the members. Its monthly publication permits up-to-the-minute data and its special departments long have been of interest to the membership of the Society. It is now also an important source of revenue.

Acting on recommendations of the Publication Committee, the Board authorized a change in the manner of distribution of TRANSACTIONS intended to bring to members in much shorter time all convention papers and discussions. Instead of quarterly issues, TRANSACTIONS hereafter will be published in two volumes as soon after the Annual Meeting as is practicable. Both volumes will appear at one time; probably this will be in the month of January following the October Annual Meeting. The magnitude of the task of bringing out at one time the convention papers is illustrated by the size of the last four quarterly issues of TRANSACTIONS, which had a total of over 1450 printed pages.

### *Educational Service*

Most of the Chapters continued their usual educational activities relating to general metallurgy, metallography, alloy steels, inspection of metals, etc. In some cases expansion was noted due to demands arising out of the nation's war efforts.

During the past few months your President was commissioned by the Board to appoint a special Advisory Committee on Metallurgical Education. Its formation developed from recognition that the training of metallurgical engineers in the United States was being curtailed. Programs sponsored by the Army and the Navy now require most of the facilities of the engineering schools of the country, but the plans make little or no provision for metallurgical training.

The Committee, comprising educators, industrialists, and metallurgists, was formed to secure facts relative to metallurgical education; to survey the industry's requirements for metallurgical engineers, both now and in the future; to determine, in the light of such information, whether representations should be made to appropriate authorities for expansion in the training of men as metallurgical engineers; and, if practicable, to furnish suggestions on post-war re-establishment of metallurgical educational activities. A report from this Committee is expected in the near future.

The three-reel educational film "Metal Crystals" produced last year has been in much demand. It has been exhibited before no less than 54 groups including Chapters, educational or industrial groups.

### *Metals Handbook*

The Presidents of your Society repeatedly have recorded the high standing of the NATIONAL METALS HANDBOOK, covering a compilation of information exceeding about 1800 pages. Several editions and numerous reprintings have been issued during the past twenty years. Since the war began, with stimulation of activity in metals, a sufficiently large demand for this encyclopedia of information arose to exhaust the supply. This year, therefore, it became necessary to reprint the METALS HANDBOOK. The new copies duplicate the last edition and are not a revision of the former book because of the high rate of obsolescence of technical data in war-time. Furthermore, those best able to revise the HANDOOK—and many members of the Society are contributors—are engaged directly in war

activities from which they would have to be detached in doing such a comprehensive job.

### *War Aids*

The industrial pattern in a war period seldom is static and it was, perhaps, to be expected that the National Emergency (N.E.) steels sponsored jointly by the government and the industry would be subject to change. As a result the Society's Guidebook to the N. E. Steels had to be completely revised. The new edition totalling 74 pages found broad acceptance and in the opinion of the editors of the bulletin and the officers of the Society rendered a war-time service to the government and to the industry.

The War Products Advisory Committees formed by more than 41 Chapters last year to assist those undertaking new work with metals continued to function effectively in many areas. While the extent of these services could be expected to decrease with a broadening of experience on the part of new organizations, the available records indicate that these advisory committees have continued to perform a useful role.

### *National Metal Congress*

Attendance at the Metal Congress in Cleveland in October 1942 was unusually large and included a good representation from all sections of the country. Exhibits were supplemented by technical sessions and War Production Conferences, at which the theme of "Aids to Production" and such other important matters as conservation of our resources were emphasized.

Of two hundred and twenty-five men invited to contribute to the group meetings, over 95 per cent accepted and participated in these off-the-record sessions. Thirty-seven papers were preprinted, presented and discussed at the regular technical meetings.

Each day just before noon special meetings were held at which members heard addresses by military and civilian leaders.

Several popular and informative talks on metals were broadcast over the air and the local press recorded the outstanding events of each day.

### *General Comments*

Looking backward, one can see that the uncertainties of a war-time period principally have had the effect of offering the Society

greater opportunities for service, not only to its members, nor solely to local communities, but to the Nation. It is a tribute to the founders and to those who, in succeeding them, helped to form the pattern of the present organization that the Society is sufficiently versatile, is closely tuned to respond to changes and has in its membership the experience and ability to take advantage of such opportunities.

May I suggest as an explanation two factors which seem to me to be of great importance. The American Society for Metals offers to its members opportunity—to learn, to teach, to discuss and to share. But with this is a desirable continuity of experienced management embodied in the present method of selection of your Board of Trustees. These features all should be preserved.

Nowhere else is the value of continuity of experience shown better than in the office of our National Secretary. May I remind you that this year marks the completion of twenty-five years of continuous service to the Society by W. H. Eisenman. To him belongs, in large part, credit for the present high standing of your Society; and on your behalf may I express appreciation to him and the hope that he will continue to serve in his present capacity for many years more.

I take pleasure, on behalf of the American Society for Metals, in expressing appreciation to the cooperating Societies for their participation in this National Metals Congress and the War Conference Displays in Chicago. They are: The Iron and Steel Division and the Institute of Metals Division of the American Institute of Mining & Metallurgical Engineers, The American Welding Society, and the Wire Association.

The Society's thanks are extended to the authors of the technical papers on our own program and those of the cooperating Societies; also to the many participants in the war production meetings and to those speakers at the Victory sessions held at 11:30 A. M.

The benefits to our war effort of interchange of information, experiences and ideas, at gatherings such as these, should be apparent to all of those who have contributed to the programs.

On my own behalf, as well as for the Society, I wish to express appreciation for the splendid cooperation of the staff at National Headquarters, the Officers of the various Chapters, the members of National Committees, and to participants in the War Conference Displays. Finally, I wish to thank the members of the Board of Trustees for their wholehearted support and their effective work.

The Society moves forward.

## TREASURER'S REPORT

FRANCIS B. FOLEY, *Treasurer*

The Society's achievements during the past year reached new peaks in every field of endeavor and are reflected in the healthiest financial condition it has ever known.

For the first year in its history the operations of the Society have produced a net gain reaching into six figures. Income to August 31, 1943, was $592,686.49 with expenses of $450,225.63 resulting in a favorable balance of $142,460.86. Income in dues from the largest membership the Society has had amounted to nearly $179,500 of which $72,257.00 was returned to chapters. Receipts from dues compare with $150,000 for last year.

METAL PROGRESS proved to be the largest revenue-producer with a net balance of $69,475.85. The new printing of METALS HANDBOOK netted about $14,000 and sales of books provided net income of about $23,000. These undertakings of your Society all showed very substantial gains over previous years. Another source of revenue was the Cleveland Metals Exposition which netted a return of $29,000.

It has been possible to increase the investments of the Society by about $143,000 or roughly 42 per cent during the year. About $19,000 of weak bonds were sold and purchases to the extent of $162,000 were made during the year, so that our present investment portfolio including purchases up to the time of this meeting may be summarized as follows in round numbers:

| | | | |
|---|---|---|---|
| BONDS | U. S. Government | $183,000 | |
| | Canadian | 8,000 | |
| | Railways | 16,000 | |
| | Public Utilities, etc. | 50,000 | $257,000 |
| STOCKS | | | $233,000 |

Investments in United States Government War Bonds increased from 32 to 37 per cent of the portfolio. Bonds now account for 52.4 per cent of the security holdings with stocks reduced from 50 per cent a year ago to 47.6 per cent of the present invested capital. Present market value of securities in the portfolio is practically equal to the cost of the securities, so that our auditors who a year ago advised increasing our reserve for depreciation by $10,000 today recommend

## CONDENSED AUDITED BALANCE SHEET

**As of August 31, 1943**

| | |
|---|---|
| **ASSETS** | |
| Cash | $ 99,873.40 |
| Securities | 489,440.68 |
| Accounts Receivable | 24,335.37 |
| Inventories | 40,532.31 |
| Other Assets | 2,948.16 |
| Real Estate | 48,450.31 |
| Office Furniture, Fixtures and Equipment | 13,859.97 |
| Deferred Charges | 26,903.11 |
| | $746,343.31 |
| **LIABILITIES AND SURPLUS** | |
| Accounts Payable | $ 29,194.37 |
| Reserves | 120,000.00 |
| Deferred Income | 9,780.00 |
| Surplus | 587,368.94 |
| | $746,343.31 |

## INCOME AND EXPENSE STATEMENT

**Year Ended August 31, 1943**

| | | | |
|---|---|---|---|
| **INCOME** | | | |
| METAL PROGRESS | | $253,007.90 | |
| Memberships | | 108,166.84 | |
| 1942 Convention—Cleveland | | 98,622.80 | |
| National Metals Handbook | | 37,138.65 | |
| TRANSACTIONS | | 6,178.18 | $503,114.37 |
| Books published | | | 60,641.53 |
| Interest and dividends | | | 16,154.37 |
| General reprints | | | 7,149 80 |
| Discount earned | | | 3,308.86 |
| Books purchased for resale | | | 558.89 |
| THE REVIEW | | | 107.65 |
| Sundry | | | 1,651.02 |
| TOTAL INCOME | | | $592,686.49 |
| **EXPENSES** | | | |
| METAL PROGRESS | $183,532.05 | | |
| 1942 Convention—Cleveland | 69,473.70 | | |
| Books published | 37,477.02 | | |
| TRANSACTIONS | 32,875.11 | | |
| National Metals Handbook | 23,410.03 | | |
| Secretary's office | 18,538.23 | | |
| Membership | 14,375.92 | | |
| General expense | 14,078.74 | | |
| Accounting department | 9,793.02 | | |
| THE REVIEW | 6,138.49 | | |
| Headquarters | 5,575.35 | | |
| Trustees' expense | 3,663.03 | | |
| President's office | 3,536.02 | | |
| National committees | 1,493.52 | $423,960.23 | |
| Annuity purchased for officer | | 16,320.18 | |
| General reprints | | 3,817.15 | |
| National defense research—War Products Advisory Committee | | 2,375.22 | |
| Loss on disposal of securities | | 1,759.99 | |
| Lectures | | 604.64 | |
| Books purchased for resale | | 493.22 | |
| Emblems purchased for resale | | 254.54 | |
| Medal fund expense | | 225.68 | |
| Books for library | | 214.78 | |
| Medals and awards | | 200.00 | |
| TOTAL EXPENSES | | | 450,225.63 |
| NET INCOME | | | $142,460.86 |

In our opinion, the accompanying balance sheet and related statements of income and expense and surplus present fairly the position of the American Society for Metals at August 31, 1943, and the results of its operations for the year, in conformity with generally accepted accounting principles applied on a basis consistent with that of the preceding year.

ERNST & ERNST
Certified Public Accountants

that we wipe out all such reserves. This has been the result of careful and continued study of the market with a view to providing the greatest security for the invested funds of the Society. These funds are in the nature of a trust built up by the membership of the Society over a period of twenty-five years, which your trustees feel it a duty to protect. Together with about $89,000 cash on hand they would yield just about $1.00 per member based on a return of 3 per cent.

Local chapters report assets totalling $116,921 or nearly $7.00 per member, compared to $98,057 of assets a year ago.

The sound counsel of the Society's finance committee, particularly that of Past-President Jeffries and Vice-President-Elect Van Horn, and that of its fiscal agent, the Cleveland Trust Company, through its Vice-President, Mr. Horner, the personal advice of the members of the board of trustees, together with the twenty-five years of exceptionally able and faithful management of the Society's affairs by its Secretary, Mr. Eisenman, have combined to bring its financial position steadily forward with increases in services to its members to the present enviable and sound status of which its members may be justly proud.

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## ANNUAL REPORT OF THE SECRETARY

WILLIAM H. EISENMAN, *Secretary*

The American Society for Metals on October 1, 1943, had a membership of 17,095. Of this number 15,305 or 88.2 per cent were the member classifications; 1057 or 6.2 per cent were sustaining members; while 710 or 4.2 per cent were juniors. There are 23 honorary and founder members.

On October 1, 1942, the Society had a total membership of 14,645. The membership this year showed a gain of 16.7 per cent.

### *Transactions*

Since the last annual meeting of the Society, there have been published four quarterly issues of the TRANSACTIONS, i.e., December 1942, March, June and September, 1943. In these four issues there were printed 1458 pages constituting 50 articles together with their discussions. A total of 40,635 TRANSACTIONS were distributed to the membership. During the year all of the papers presented at the

1942 Convention in Cleveland will have been published in their entirety together with others received during the year.

### *Metal Progress*

Statistically and financially, METAL PROGRESS has completed an unprecedented year. Editorial pages for 1943 fiscal year, totalling 688, are close to the steady average since 1937 (650 pages). Revenue advertising, however, has made a large advance—an increase of 25 per cent over the record-breaking volume of fiscal 1942—to a total of 1595 pages. The result is that the largest magazine in A.S.M. history had the largest circulation (average monthly figures being 17,060 copies of a 204-page book). This has made it necessary to "borrow" paper from TRANSACTIONS, reduced in circulation voluntarily by members, in order that the Society as a whole might stay within the permissible consumption of paper, which had to be cut 10 per cent below 1942. It has also required METAL PROGRESS to reduce its page size from the "de luxe" 9½ by 12⅝ inch to the standardized 8⅛ by 11¼ inch. Certain typographical readjustments as to type-size and column-width have enabled the editor to place the same number of words on a single page without too much sacrifice in appearance or legibility. Unfortunately it has also been necessary to reduce the thickness (weight) of the paper sheet, which has also reduced its opacity, substantial feel, and printing quality. The membership is asked to bear with these emergency matters as items which will be corrected at the earliest possible moment.

A new department called "Bits and Pieces" was started in July 1942, to contain minor items about labor-saving devices in laboratory or shop, or brief discussions of metallurgical theory. It has proven very popular. The "Metallurgical Catalog" or "Where-to-buy List" published semi-annually since January, 1941, has been issued this year as a separate section. The department on "War Products Consultation" has appeared at infrequent intervals, due to the difficulty in securing worth-while material that would pass the Censor. In other respects METAL PROGRESS has carried on in the way our members have a right to expect from past performance.

Thanks of the Board are due to the large number of members and friends who have contributed their time to achieve this end. Credit is also due to the editorial and business staff, who have carried on so ably.

*Handbook*

As reported last year, it will be necessary, after the war, to make many important revisions in HANDBOOK articles so that information and data on new practices, methods, and materials can be incorporated in the HANDBOOK. Also the members are so busy with war production they have little time to serve on committees for the preparation of HANDBOOK reports.

Because of these conditions, the Board of Trustees decided that a new HANDBOOK should not be re-edited until after the War. Therefore, the HANDBOOK Committee, its Subcommittees, and authors have been quite inactive during 1943.

Even though the HANDBOOK Committee and its Subcommittees are inactive, they are organized and set up for work, and can start functioning at any time their services are required. The personnel of the HANDBOOK Committee is as follows:

G. V. Luerssen, Chairman; E. C. Bain, A. L. Kaye, J. T. MacKenzie, H. D. Newell, N. I. Stotz, Lyall Zickrick (A.I.M.E. Rept.), A. J. Herzig, C. H. Lorig, H. L. Maxwell, C. W. Obert, G. T. Williams, and J. E. Donnellan, Secretary.

At the close of 1942, R. S. Archer, Chairman; H. B. Pulsifer, A. P. Spooner, and Dr. R. F. Mehl completed their term of membership on the HANDBOOK Committee, so were retired from the Committee's personnel. These men contributed much to the planning and organizing of the HANDBOOK. The important work and loyal services given the HANDBOOK Committee by these men are greatly appreciated by the Society.

Some of the Subcommittees of the METALS HANDBOOK Committee have formulated a plan, and in a few instances, have projects in preparation. However, in the majorty of cases, the Subcommittees are only remaining as standing committees waiting for the proper time to prepare their report and practices.

The Subcommittees that have been organized to date are as follows:

Subcommittee on Alloying Elements
- Master Property Chart
- Softening Curves
- Hardenability of Alloy Steels
- S-Curves

Subcommittee on Constitutional Diagrams
Subcommittee on Cladding
Subcommittee on Conditioning Semi-Finished Steel (Article Completed)

Subcommittee on Definitions
Subcommittee on Properties of Forgings in Heavy Sections
Subcommittee on Hardenability
Subcommittee on Mechanical Testing
Calibration of Testing Apparatus
Testing Castings
Compression Tests
Creep Tests of Metals
Fatigue and Corrosion Fatigue
Testing Forgings
Hardness Testing
Introduction to Mechanical Testing
Notch Bar Testing
Testing Plate, Shapes, and Bars
Testing Pressure Vessels
Testing Rod and Wire
Testing Sheet and Strip
Test Specimens; Preparation of
Tensile Testing
Torsion Testing
Testing Tubular Products
Testing Welds
Subcommittee on Powder Metallurgy
Subcommittee on Specifications
Subcommittee on Tool Steels

The Nonferrous Data Sheet Committee of the American Institute of Mining and Metallurgical Engineers, and the Committee on Welding and Cutting organized by the International Acetylene Association are also organized and ready to again cooperate with the HANDBOOK Committee in the preparation of a new edition of the HANDBOOK, when the proper time comes.

Both of these Committees have always cooperated in a most splendid manner with the HANDBOOK Committee. Their cooperation is much appreciated by all. The personnel of these Committees is as follows:

*Nonferrous Data Sheet Committee*—Lyall Zickrick, Chairman; E. W. Palmer, K. R. Van Horn, Carl E. Swartz, Dr. Frederick N. Rhines, and Mr. Gerald Edmunds.

*Welding and Cutting Committee*—C. W. Obert, Chairman; C. L. Altenburger, Roger W. Clark, E. V. David, Charles H. Jennings, H. L. Maxwell, and H. R. Morrison.

A second printing of the 1939 edition of the METALS HANDBOOK was made the latter part of last year. This second printing ran 15,000 copies. Already 7069 copies of the second HANDBOOK printing have been distributed. This is again proof of the popularity of METALS HANDBOOKS throughout the metals industry.

### *The Review*

During the past year THE REVIEW has continued to use the size and format adopted in August 1942. This has provided an increase of 35 per cent in the amount of space available. Of the 7040 column-inches printed in ten issues during the year (July and September omitted), 13.9 per cent was devoted to advertising, particularly of A.S.M. books. Reports of chapter meetings and activities occupied 41.5 per cent of the space.

Most of the A.S.M. chapters have appointed reporters to send in accounts of their meetings and activities regularly. The assistance of these men in providing good material for publication has been an important factor in the success of THE REVIEW as a central source of information on all aspects of chapter activities, doings of members, and national affairs.

The October issue was increased in size from 8 to 16 pages, and was devoted entirely to the National Metal Congress and War Conference Displays. It had a circulation of 46,000 among the members of the cooperating societies in the Congress and other technical organizations.

### *Preprints*

Thirty-seven papers were presented before the Twenty-fourth annual Convention held in Cleveland last year, all of which were preprinted. For this year's Convention in Chicago, 35 papers have been scheduled for presentation and all of these likewise have been made available in preprint form. The total number of pages for the 1943 preprints is 840. A total of 26,925 preprints has been distributed free to the membership to date.

### *Books*

Since the Cleveland Convention last year, only one book has been in process of publication, i.e., "Tool Steels" by J. P. Gill and co-authors, R. S. Rose, G. A. Roberts, H. G. Johnstin and R. B. George. This book contains some 577 pages, 277 illustrations and will be available shortly.

The demand for Society published books during the past year has been very gratifying. More than 19,335 books of all titles were sold during the last year. This number is exclusive of the HANDBOOK and N.E. Steels pamphlet.

### *Publication Committee*

The Publication Committee for the year 1942-43 was made up of the following: M. Gensamer, Chairman; J. B. Austin, R. M. Brick, Walter Crafts, T. G. Digges, E. H. Dix, Jr., A. E. Focke, W. R. Frazer, Walter E. Jominy, E. G. Mahin, Gilbert Soler, Clair Upthegrove, T. S. Washburn, S. P. Watkins, and L. L. Wyman, and Ray T. Bayless, Secretary.

Throughout the year and up to the present time the Committee has reviewed and approved 37 papers, rejected 3, and is in the process of reviewing three.

The last meeting of the Publication Committee was held in National Headquarters office in Cleveland on July 30th, 1943. This meeting was concerned with the arrangements of the technical program for this Convention.

### *Educational Committee*

The Educational Committee for the year 1943 was made up of the following personnel: C. W. Mason, Chairman; J. L. Bray, O W. Ellis, J. G. Jackson, J. T. Norton, B. R. Queneau, T. H. Wickenden, and Ray T. Bayless, Secretary.

The Committee has held no meetings this year due to the fact that the first phase of the motion picture film on "Metal Crystals" has been completed at Ohio State University and that further work on this film has been delayed due to lack of personnel at that University. It is probable that no additional work can be done on motion pictures for the duration.

Due to the fact that afternoon and evening periods at this year's Convention have been set aside for War Conference discussions, it was previously decided that educational lectures for the present Convention would not be included; thus there was no need for a meeting of the Committee.

The Committee is indeed gratified to know of the marvelous response of the chapters in the use of the 3-reel motion picture, "Metal Crystals" which was made available a year ago. Up to the present time it has been shown before 54 groups which include chapters and other industrial and educational groups.

The Committee has discussed by mail the feasibility of making available blow-ups of data sheets and pertinent metallurgical infor-

mation for the benefit of teaching groups. These would be wall charts of rather large size for use in class-rooms with note-book size reproductions available to individual students. This phase of the visual education has been approved by the Committee and will be publicized in early issues of THE REVIEW.

### *War Conference Displays*

The War Conference Displays represent a departure from the National Metal Exposition which usually occupies the largest exhibit hall available in a metropolitan center.

This is the second time the exhibits have been held in a hotel, the first being in the Stevens Hotel in 1930. The fact that the Palmer House was originally constructed with the 7th, 8th and 9th floors devoted to sample rooms has been instrumental in indicating the ease and adaptability with which the War Conference Displays have fitted into the hotel.

It has been decided by the Board of Trustees that the National Metal Congress and the War Conference Displays for 1944 will be held in Cleveland the third week in October (October 16th to 20th inclusive), with the War Conference Displays being held in the vast exhibit halls of Cleveland's Public Auditorium.

Twice now the National Metal Congress and the War Conference Displays have been held when our country was in war, and both Congresses have shown themselves beyond all doubt to have been helpful to the members, to industry and to the country.

The thousands who have been in attendance at the last two conferences, together with their determined eagerness to secure the latest information on their immediate problems, have placed an additional emphasis on the importance of these occasions.

### *National Metal Congress*

Four national technical societies have again given their hearty cooperation in the presentation of the present Metal Congress. The technical programs are of outstanding merit and of great current interest, making a valuable contribution to the war.

One of the outstanding features of the Congress has been the A.S.M. group meetings on production, conservation and post-war planning, which this year, as for the last two, have occupied the afternoon and evening sessions during convention week.

This type of meeting, originated first by the A.S.M. and now used extensively, has in subject matter achieved an enviable reputation for the discussion of problems of current and immediate interest.

It has been a source of extreme pleasure to all those participating in the planning of this program to observe the hearty cooperation and acquiescence given by the experts invited to participate. They are all entitled to a citation for their contribution to the war effort.

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## ANNUAL MEETING OF AMERICAN SOCIETY FOR METALS

*Chicago, Wednesday, October 20, 1943*

The meeting was called to order by President French, who announced that the first order of business was the President's report. He then invited Vice-President Grossmann to take the chair while he read his address. This is published in full beginning on page 12 of this volume of TRANSACTIONS.

VICE-PRESIDENT GROSSMANN: You have heard the report of the national President. There being no comments the report will stand as read. I now return the chair to the President.

PRESIDENT FRENCH: The next order of business will be the annual report of the Treasurer, Mr. Francis B. Foley.

. . . Treasurer Foley presented his report which appears in full beginning on page 18.

PRESIDENT FRENCH: You have heard the report of the Treasurer. There being no objections it will stand as read. The next order of business is the report of the Secretary.

. . . The Secretary presented his report which appears in full beginning on page 20.

PRESIDENT FRENCH: You have heard the report of the Secretary. There being no comments the report will stand as read.

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## ELECTION OF OFFICERS

PRESIDENT FRENCH, *Presiding:* Complying with the Constitution, I appointed on March 16, 1943, the following Nominating Com-

mittee, selected from the list of candidates suggested by eligible chapters prior to March 1, 1943.

Chairman, T. S. Fuller, Schenectady Chapter.
J. W. Queen, Jr., New Jersey Chapter.
H. W. McQuaid, Detroit Chapter.
C. E. Swartz, Cleveland Chapter.
Roy Atwater, Muncie Chapter.
R. W. Schlumpf, Texas Chapter.
C. M. Inman, Worcester Chapter.

The Committee met in New York on Tuesday, May 18, and made the following nominations:

President—M. A. Grossmann, Carnegie-Illinois Steel Corp., Chicago—1 year
Vice-President—Kent R. Van Horn, Aluminum Co. of America, Cleveland—1 year
Treasurer—Harry D. McKinney, Driver-Harris Co., Harrison, N. J.—2 years
Trustee—C. H. Herty, Jr., Bethlehem Steel Co., Bethlehem, Pa.—2 years
Trustee—A. L. Boegehold, General Motors Research Laboratories, Detroit, Mich.—2 years

A report of these nominations duly appeared in THE REVIEW of May, 1943.

I have been informed by the Secretary that no additional nominations were received prior to July 15, 1943, for any of the vacancies occurring on the Board of Trustees. Consequently the nominations were closed. I shall now call upon the Secretary to carry out the provisions of the Constitution in respect to the election of national officers.

W. H. EISENMAN, *Secretary*: Conforming with the provisions and requirements of the constitution of the American Society for Metals, I hereby cast the unanimous vote of the members for the election of the aforenamed candidates who were regularly nominated May 18, 1943.

PRESIDENT FRENCH: The provisions of the constitution having been complied with, I hereby declare the candidates heretofore named to be duly and unanimously elected to the several specified offices, the terms of each beginning on the day following the close of this annual meeting.

. . . President French then introduced the newly-elected trustees, Mr. McKinney, Mr. Boegehold and Mr. Herty, and Vice-President-Elect Van Horn, and President-Elect Grossmann.

Dr. Grossmann said a few words to the audience.

. . . President French then presented certificates to: Mrs. B. W. McGillivray for 10 years' service as secretary of Montreal Chapter; to Mr. Alexis Caswell for 20 years' service as secretary of Northwest

Chapter; and to Mr. H. L. Walker for 20 years' service as secretary of the Pittsburgh Chapter.

PRESIDENT FRENCH: Has anyone present anything to bring before the meeting for the benefit of the Society? If not, a motion to adjourn is in order. Meeting adjourned.

. . . Following the annual meeting, President French introduced Dr. C. H. Mathewson, Yale University who presented the Eighteenth Campbell Memorial Lecture. In presenting Dr. Mathewson President French said—

The 1943 Campbell Lecturer, chairman of the Department of Metallurgy, Yale University, came to the faculty in 1907 as instructor in chemistry and metallography. Himself a Sheffield graduate (1902) he was fresh from advanced study under Professor Tammann in Germany, who was then pioneering in the systematic study of metallography. In New Haven it was not until 1911 that the routine of teaching freshman chemistry was broken and courses on microscopic metallography and the constitution of alloys were firmly established. Meanwhile, Dr. Mathewson had translated Ruer's "Elements of Metallography" (pretty strong stuff even yet).

The first World War brought calamity to the growing Department of Mining and Metallurgy, housed in a new and excellent laboratory, the gift of John Hays Hammond. At the time of the Armistice, Dr. Mathewson was the sole survivor of a notable faculty. The calamity was, however, merely an opportunity to start off afresh. Obviously metallurgy rather than mining was the important study for post-war students at Yale. Product metallurgy was the vital aspect rather than chemical metallurgy of ore dressing and smelting.

Based on these principles, the new chairman of the Department of Metallurgy has built a curriculum and faculty that have attracted to Yale a steady stream of men for both undergraduate and advanced instruction—a stream that is measured not in members but in quality best judged by Zay Jeffries' recent remarks, "Among those students are some of America's and the world's most able metallurgists". These students have formed a most active group, formally called the Yale Metallurgical Alumni Association, and by some in respectful haste "Matty's Mob". This group has held many meetings throughout the years to assist in departmental affairs and on the occasion of Dr. Mathewson's 60th birthday staged a party at which a fitting volume of technical papers was dedicated to their friend and teacher.

Professor Mathewson's evolution since 1907 may be traced by his numerous scholarly publications embracing many fields of metallurgy such as the phase relationships in alloy systems, the effects of rolling mill practice and heat treatment on the properties of copper alloys and the plastic deformation of zinc, copper and iron. One of the most notable contributions on the latter subject was the 1928 Institute of Metals lecture on "Twinning of Metals". His efforts have been rewarded by the James Douglas Medal "for his scientific contributions to the art of working and annealing nonferrous metals".

As a friendly human being, many besides his students bear witness. He is a member of many engineering societies and important technical committees. He has given freely of his advice on many governmental advisory boards.

Dr. Mathewson is a traveler of note, and recently has concentrated on our national parks. His color travel movies and stories have supplied the entertainment for intimate friends on cold wintry nights in New Haven. In fact, I am informed that the Professor has even resorted to the discomfiture of riding western mules to secure unusual shots.

It is with a great deal of pleasure that I introduce the President of the American Institute of Mining & Metallurgical Engineers, Dr. Champion Herbert Mathewson, as the 1943 Campbell Memorial Lecturer, who will speak to you on the subject of "Structural Premises of Strain Hardening and Recrystallization".

The lecture is printed in full in this volume of TRANSACTIONS beginning on page 38.

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## THE ANNUAL DINNER

The Annual Dinner taxed to capacity the food and labor facilities of the Palmer House, and ticket sales had to be stopped after 1050 seats were reserved.

Those seated at the speakers' table were: Dr. Franklyn B. Snyder, president, Northwestern University; Admiral Alex M. Charlton, U. S. Navy, director of the Office of Inspector of Naval Material, Chicago District; Col. John Slezak, deputy chief of the Chicago Ordnance District; Edward T. Lawless, president, Palmer Houses Company; Dr. Harold Vagtborg, director, Armour Research Foun-

dation; Walter E. Hadley, manager of operations, Chicago district; Carnegie-Illinois Steel Corp.; Fred J. Robbins, technical director, Plomb Tool Co., and chairman, Chicago Chapter of the A.S.M.; T. L. Haines, engineer of the Vascoloy-Ramet Corp., and secretary, Chicago Chapter of the A.S.M.; John B. Hughes, Mutual Broadcasting Commentator; Shadburn Marshall, research metallurgist, Remington Arms Co., and recipient of the 1943 Henry Marion Howe Medal; Zay Jeffries, chairman of the board, Carboloy Co., honorary member and past-president (1929), A.S.M., and recipient of the Gold Medal of the American Society for Metals; Roy Arthur Hunt, president, Aluminum Co. of America, and recipient of A.S.M. Medal for the Advancement of Research; William P. Woodside, chairman of the board of the Park Chemical Co., and a founder member and a past-president (1939) of the A.S.M.; Col. Albert E. White, director, department of engineering research of the University of Michigan, and founder member and a past-president (1921) of the A.S.M.; Herbert J. French, president of the American Society for Metals, and assistant manager of the development and research division of the International Nickel Co., Inc.; Francis B. Foley, superintendent of research of the Midvale Co., and treasurer of the A.S.M.; W. H. Eisenman, secretary, A.S.M.; M. A. Grossmann, director of research, Chicago District, Carnegie-Illinois Steel Corp., and president-elect of the A.S.M.; Kent R. Van Horn, research metallurgist of the Aluminum Co. of America, and vice president-elect of the A.S.M.; Harry D. McKinney, vice-president of the Driver-Harris Co., and treasurer-elect of the A.S.M.; A. L. Boegehold, head of the metallurgy dept. of the research laboratory division of the General Motors Corp., and trustee-elect of the A.S.M.; Erle G. Hill, assistant general supt. of the Gary Works of Carnegie-Illinois Steel Corp. and trustee of the A.S.M.; V. N. Krivobok, chief metallurgist of the Lockheed Aircraft Corp., and trustee of the A.S.M.; Norman F. Tisdale, metallurgist of the Molybdenum Corp. of America, and a trustee of the A.S.M.

The main address was given by John B. Hughes, nationally known news commentator, whose subject was "The Far East", a timely and well-presented discussion of the Japanese military and political situation.

His talk was followed by the presentation of the Sauveur Achievement Award to Charles H. Herty, Jr.; of the Howe Medal to Shadburn Marshall; of the newly created Gold Medal of the

American Society for Metals to Dr. Zay Jeffries; of the new A.S.M. Medal for the Advancement of Research to Roy A. Hunt; and of a founder membership and an annuity to Secretary W. H. Eisenman in recognition of his 25 years of service to the Society.

### *Presentation of Sauveur Achievement Award*

In 1934 the Society established its second award, consisting of a plaque and certificate, in honor of Dr. Albert Sauveur, a distinguished metallographist and for many years an honorary member of the Society. This medal was established during the lifetime of Dr. Sauveur, who was, himself, the first recipient.

The purpose of the award is to recognize a metallurgical achievement which has stood the test of time and stimulated others along similar lines to the extent that a marked and basic advance has been made in the metal arts and sciences.

The recipient is selected by the past presidents of the Society, of which there are now eighteen. The award this year has been made to Dr. Charles H. Herty, Jr., Assistant to Vice-President, Bethlehem Steel Co., Bethlehem, Pa.

Before the time when he began his work on the physical chemistry of steelmaking, two aspects in this field were hampering progress. On the scientific side, developments were dominated by the metallographist and the analytical chemist; on the practical side, difficulties were encountered because steelmaking stretches the capacity both of men and materials beyond their ordinary limits.

In Dr. Herty the steel industry found an able technician and a leader of men. His success is measured not only by the results of his own researches but by those coming from his stimulation of others.

Due to illness which prevented Dr. Herty's attendance at the meeting Mr. Rufus S. Tucker, manager of sales of the Bethlehem Steel Co., received the certificate and plaque for Dr. Herty.

### *Presentation of Howe Medal*

In 1922 the Society established the first of its medals in honor of one of its first honorary members, the late Dr. Henry Marion Howe, distinguished scientist, often called the dean of American metallurgists.

In establishing the medal, provision was made that it should be awarded to the author of the paper judged of highest merit, pre-

sented before the A.S.M. and published during any one year in the TRANSACTIONS of the Society.

The medal for 1943 has been awarded to Dr. Shadburn Marshall, Research Metallurgist, Remington Arms Co., for his paper entitled "The Carbon-Oxygen Equilibrium in Liquid Iron" which was published in the September 1942 issue of the Society's TRANSACTIONS.

### *Conferring of Gold Medal of A.S.M.*

The Gold Medal of the A.S.M. recognizes outstanding metallurgical knowledge and a mature ability in the diagnosis and solution of diversified metallurgical problems. Dr. Jeffries, the first recipient

*The Gold Medal of the American Society for Metals*

of the medal, is chairman of the board of the Carboloy Co., technical director of the Lamp Department of the General Electric Co., scientist, author, administrator, and a past president of the Society. The medal was accompanied by a certificate bearing the following citation:

> Zay Jeffries, recognizing the practical importance of the grain size in metals, devised procedures for its measurement and control. His utilization of these concepts and methods has resulted in: generally beneficial improvements in the manufacture and application of tungsten wire, the clarification of the mechanism of the hardening of steel, and a better understanding of the significance of grain size relations to the properties and fabricating characteristics of metals at elevated temperatures.

Zay Jeffries established the importance of the time factor in diffusion reactions in coarse structures. This led him to the development and commercial application of heat treatable aluminum casting alloys. His elucidation of the effects of the various constituents on the forgeability and strength of aluminum alloys brought about the discovery of commercially workable alloys which are the basis of the present aluminum forging industry. The metallurgical principles indicated were combined in the general slip interference theory of the hardening of metals which has inspired widespread and profitable metallurgical research.

Zay Jeffries' belief in the potential need for better cutting materials and the latent possibilities of hard carbides prompted his perseverance in the organization of a sound developmental program, the pursuance of which matured into the present commercial utilization of these materials in the working industry.

*Conferring of A.S.M. Medal for the Advancement of Research*

The A.S.M. Medal for the Advancement of Research gives tangible recognition to the importance of research and the benefits which may be derived from it in the metal industries. The first

*The A.S.M. Medal for the Advancement of Research*

recipient of this medal was Roy Arthur Hunt, president of the Aluminum Co. of America. The citation on the certificate accompanying this medal was as follows:

Growing into a position of executive responsibility in the Aluminum Company of America about 25 years ago, Roy Arthur Hunt found that notable predecessors in the persons of Hall, the inventor, and Hoopes, the engineer, had developed the processes for the production of pure aluminum to such a position that ample and increasing quantities were being put to man's use. Despite the apparently satisfying situation, Roy Hunt and his associates felt that if this relatively soft metal could be appreciably strengthened its use could be expanded and diversified. Many attempts to produce strong alloys in the plants had brought nothing but failure; the problem required extensive research directed toward practical ends, and this was initiated forthwith by the establishment of Aluminum Research Laboratories.

Roy Hunt's support, through prosperous and adverse years alike, of these Laboratories has been constant and unfailing. A large number of strong alloys, heat treatments, and processes, have been developed, resulting in many combinations of useful engineering properties. The vision of a greatly expanded strong aluminum alloy industry was realized in time to provide the main structural elements for the present enormous aircraft production program. A large group of technical experts had been assembled and were available to aid in the necessary seven-fold expansion of aluminum reduction and fabrication capacity to meet the needs of the present emergency. Likewise the fundamental principles evolved during the research on aluminum have contributed to the solution of metallurgical problems in other fields. Finally, the entire metal industry has gained inspiration from this courage and faith in research.

*Conferring of Founder Membership and Presentation of Annuity*

The recognition and tribute to National Secretary Eisenman in conferring upon him a founder membership in the A.S.M. was expressed in the following words of President French:

"This marks the close of the twenty-fifth year of service to the American Society for Metals of our national secretary, William H. Eisenman, and those who have more than a casual acquaintance with the Society will recognize the significance of this occasion. Much of the success which has been achieved

during the past quarter century has had Mr. Eisenman's deft touch if it did not stem from his foresight, imagination, energy and perseverance.

"The American Society for Metals, as is well known, is the result of the amalgamation of the Steel Treating Research Society, which was established in 1913, and the American Steel Treaters Society, which was established in 1917, resulting in the formation of what was then known as the American Society for Steel Treating and is now known as the American Society for Metals.

"Mr. Eisenman became secretary of the American Steel Treaters Society in 1917 and took office as secretary of the American Society for Steel Treating in 1920. He has served continuously as secretary since that time. Under his leadership and guidance the Society has grown from a few chapters to 62, scattered over the country from the east to the west coast and from Canada to the borders of Mexico. Membership has increased from about 1500 in 1920 to over 17,000 in 1943 and the financial condition represented by virtually no assets in 1920 has developed into a capital structure of about six hundred thousand dollars. The Society now also owns its own home at 7301 Euclid Avenue, Cleveland, Ohio.

"There is doubtless no secretary of a national society who is better known to its membership. He makes a point of visiting, with the president of the Society, a majority of the chapters every year, ascertaining their needs. He is an exceptionally able administrator; and he has ingrained himself into the hearts of those with whom he comes in contact, irrespective of their affiliations. He is cherished and beloved by all and in doing honor to him the Society does honor to itself.

"It is my pleasant duty and privilege to announce at this time that the Board of Trustees of the American Society for Metals has elected William Hunt Eisenman to Founder Membership.

"Since the Society has no pension plan, the Board has also provided an annuity for Mr. Eisenman through a Life Insurance Annuity Contract. Its purchase was made by a single payment and the funds were appropriated by the Board from dividends and interest received by the Society during the past 15 months on its investments in stocks and bonds.

"Mr. Eisenman, under the authority of the Board of Trustees and with the sincere appreciation of the members of the American Society for Metals, I hand you your certificate of founder membership and the annuity contract."

Mr. Eisenman responded as follows:

"I am deeply moved and greatly honored to be named one of the five founder members of this Society. I consider it the highest tribute, Mr. French, that the present board of trustees has deemed it fitting that I should be so honored. My contributions to the success of the A.S.M., small though they may be, have been a labor of love.

"When on yesterday Mrs. Eisenman and I received the sterling silver service as a gift from the Past Presidents of the Society, our cup was full to overflowing.

"The presentation of the annuity is a lasting indication of the thoughtfulness that the members and all the Boards of Trustees with which I have served have directed towards me and mine. The memory of these events will be with us always. They are written in our hearts forever. We never were so proud."

# STRUCTURAL PREMISES OF STRAIN HARDENING AND RECRYSTALLIZATION

By C. H. Mathewson

*Abstract*

*In this lecture an account is given of the early history of investigations which sought to clarify the macroscopic aspects of plastic deformation but failed to reveal in the slip mechanisms postulated a generally acceptable cause for strain hardening. The inadequacy of slip interference between differently oriented crystallites to meet the extreme requirement of strain hardening, as argued by G. I. Taylor on a mathematical-geometrical basis, does not take into account the possibility of unique configurations of strain at inner surfaces of fragments or crystallites.*

*A qualitative interpretation of strain hardening in the plastic extension of a single crystal is attributed to the development of residual stress though inability of strained parts of the same crystal to realize the mutually obstructive rotations which (with reference to the simple model of extension or contraction by elastic shear and rotation) would normally characterize contraction and removal of elastic shear strain on releasing the axial load. Results of grain boundary observations and measurements of the variable axis shift in different parts of variously associated grains are included.*

*It is suggested that the slipping process is far more complicated than hitherto assumed, and that an observed slip direction is merely the resultant of movements in which the atoms find paths of lower potential than the direct route over barriers set up by their own volume requirements.*

*This point of view is supported by an X-ray study of the lattice rotations of crystallites in a single crystal of aluminum strained by axial loading wholly within the range of operation of a single slip system, and by the types of rotation necessary to adjust recrystallized grains of aluminum or brass to the orientation of the original single crystal from which they were derived by annealing after a small plastic extension.*

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This is the eighteenth Edward DeMille Campbell Memorial Lecture, presented by Dr. C. H. Mathewson, professor of metallurgy, Yale University, New Haven, Conn. The lecture was presented October 20, 1943, during the Twenty-fifth Annual Convention of the Society, held in Chicago.

"IN 1920 Edward DeMille Campbell, Professor of Chemistry and Director of the Chemical Laboratory of the University of Michigan, became a charter member of the Detroit Chapter of the American Society for Steel Treating. In April, 1921, he was elected to honorary membership, being the fourth person to receive this distinction. He died on September 18, 1925. On December 5, 1925, the American Society for Steel Treating, seeking to commemorate his achievements, established the E. D. Campbell Lecture. The first lecture was given in Chicago a year ago by Dr. William Minot Guertler of Charlottenberg, Germany", and Dr. Zay Jeffries, in 1927, concluded this paragraph by acknowledging the privilege of presenting the second lecture.

Last year's lecture by Professor John Chipman was the seventeenth of the series and it is now my own privilege to add a building block to the edifice of appreciation built around the life and achievements of Professor Campbell.

I have lately spent some pleasant hours browsing through his publications, conveniently listed by Dr. Jeffries in the second lecture and, in beginning the introduction of this lecture, I found myself about to quote from the 1914 paper "A Contribution to the Theory of Hardening and the Constitution of Steel" certain expressions of Professor Campbell's philosophy regarding the need for hypotheses to express the presumed significance of accumulated experimental results, for the purpose of critically directing future studies towards the final elimination of all doubtful premises, when I realized that Dr. Jeffries had quoted elaborately from the same paper and had appropriately recognized Professor Campbell's singular devotion to high scientific ideals.

While his preferred field of study, the chemical constitution of steel, with particular relation to the role of carbides, did not yield an insight into the physical constitution of steel as it is now generally understood, his methods and deductions are worthy of study and emulation.

I have chosen the subject of strain hardening and recrystallization for this lecture because in my own thinking it lies at the root of the extraordinary versatility of our common metals and alloys. Whatever we do to them in mill or shop practice provokes a response in the form of strain; a certain disturbance and readjustment of the atoms within their structural frame of crystallinity. Much is known about crystal structure, slip systems, macroscopic movements of the

material in bulk, empirical microstructures, rates of change from one observed state to another, size of precipitated or fragmented particles produced by heat treatment or plastic deformation and there is an enormous accumulation of data on strength properties as related to specified conditions or treatments, X-ray evaluations of lattice changes, such as line displacement or broadening, but no general understanding of changes in the pattern of atomic interplay which must be responsible for the major effects, and these are indeed miracles of transformation. We seem to accept with feeble imagination the fact that a metal may be doubled in strength by merely changing its shape! Perhaps I have underestimated the thought which has gone into this bottomless pit because leaders of our science and technology have been constrained to express opinions, reaching all the way from Tammann's (G. Tammann, Z. Metallkunde, Vol. 28, 1936, p. 16) bold assumption of "an unknown change in the atoms"* through an interlude of slip interference (Jeffries) reconstructed by Taylor** into a form of interference by one system of crystal faults with the propagation of another set, to the more generalized assumption that strain hardening is hardening or resistance to slip due to some strained configuration of the atomic arrangement, not necessarily restricted to an imperfect lattice.

The confusion of all this readily appears when we seek to look into the working possibilities of unfamiliar metals such as the hexagonal metal, beryllium, which would be invaluable if we had enough of it and could make it behave plastically. It is alleged that small amounts of ductile beryllium have been prepared by sublimation (H. A. Sloman, Journal, Institute of Metals, Vol. 49, 1932, p. 365), but metal so far commercially available cannot be cold-worked. By what process of considering its hypothetical structural faults or the change which might take place in its atoms, or its capability to assume a "ductile" configuration of strain in its crystal structure can we form an opinion concerning its inherent brittleness or ductility. Beyond the fact that it presumably possesses the same major slip and twinning systems as zinc and magnesium with an axial ratio that would cause it preferentially to resemble magnesium, nothing of importance comes to mind, except recognition of the fundamental condition that ordinary cold working of this metal means

*"The elementary process in cold working is the forced gliding by plastic deformation of crystallite parts against one another . . . The friction increases with increasing movement which is to be ascribed to an unknown change in the atoms, perhaps extending to the near vicinity of the two glideplanes."

**Reference and discussion introduced later.

working at temperatures much further below the melting point than in the case of the other metals.

In this lecture no attempt will be made to give a thorough evaluation of the literature of this broad subject or to develop in detail, within the range of a platform presentation, any new theoretical point of view. In short, the purpose is not to present a scientific paper, but rather to give a provisional estimate of prevailing scientific opinion, to emphasize certain divergent attitudes of mind and to point out the need for further study of various obscure features of crystal plasticity.

## Early History of Investigation Concerning the Plastic Behavior of Metal Crystals. The Discovery of Slip Bands by Ewing and Rosenhain

The study of the plastic deformation of metals from a structural point of view had scarcely begun in the nineteenth century although certain crystallographers had observed the surface markings and angular changes associated with processes of translation or simple shear (twinning) in various minerals or even native metal crystals. (Cf. Desch, Metallography, 4th Ed., 1937, p. 269.) Forty-three years ago, at the turn of the century, Ewing and Rosenhain (J. A. Ewing and W. Rosenhain, Philosophical Transactions, Royal Society London, 1900, 193A, p. 353) described the now-familiar slip markings seen on the surface of a polished and preferably etched metal specimen after straining into the range of plastic deformation. The Rosenhain diagram, reproduced from his Introduction to Physical Metallurgy and familiar to every student of Metallography or Physical Metallurgy, is shown in Fig. 1. A few pertinent phrases from the Author's text are quoted as follows:

"The true nature of the lines is now well understood, and is summed up in the name 'slip bands' which is given to them. Their origin lies in the fact that when a crystal of a ductile metal is forcibly altered in shape, it adapts itself to the new configuration imposed upon it by a process of sliding or slip which occurs on certain of its crystallographic planes. The manner in which this occurs is well illustrated by the behavior of a pack of cards, or of a pile of books, when the pile is distorted—the shape of each individual card or book remains unchanged but the shape of the pile is changed by the sliding of the individual cards or books over one another. The process may

be made clearer by the diagram of Fig. 1 which is intended to indicate in a very approximate manner the condition of a cross section of two adjacent crystals before and after plastic straining. The upper sketch represents the unstrained crystals, whose smooth upper (polished) surface is indicated by the line ABC—the step at B is the slight difference of level between adjacent crystals formed as the result of etching; the boundary between the crystals is represented by the full line BD, while the potential planes of gliding or slip, dif-

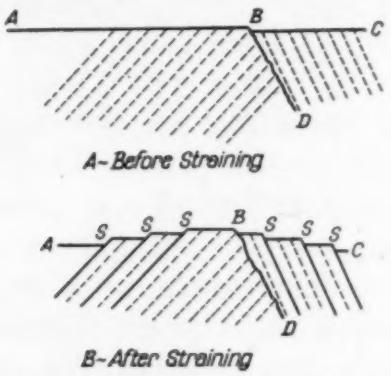


Fig. 1—Diagram of the Formation of Slip Bands. (Rosenhain)

ferently oriented in each crystal, are indicated by the dotted lines. After straining slip has taken place on some of these slip planes, and minute steps have consequently been formed in the surface at the points marked S, S, S, in the lower figure—these steps will of course slope in different directions in different crystals."

Without quoting further, it may be noted that the appearance of bands in the microscopic image is consistent with this diagram, and moreover the existence of steps, as depicted, was further demonstrated by Rosenhain through an appropriate technique of measurement on cross sections. In this way, he found steps measuring about 1/50,000 of an inch in a strained iron crystal.

Rosenhain recognized that from an atomic point of view phenomena such as strain hardening are not at all clarified in terms of a simple slipping process preserving the atomic pattern from plane to plane and it is probably well-known to this audience that he considered the slipping process to be complicated by an atomic disturbance at the adjacent slip surfaces which in its extreme pattern would no longer permit a normal crystallographic rearrangement and might therefore be termed an amorphous arrangement of the atoms in these regions.

It is my impression that scarcely any advocate of the so-called "amorphous theory" can be found among present day physicists or physical metallurgists, but it is of interest to note that J. L. Haughton who prepared a third edition of the "Introduction to Physical Metallurgy" (1935) after the death of Dr. Rosenhain, in deference to the Author's latest opinion "that he believed there was more evidence in its favor now than ever before", avoided any drastic alteration in the chapter entitled "Effect of Strain on the Structure of Metals".

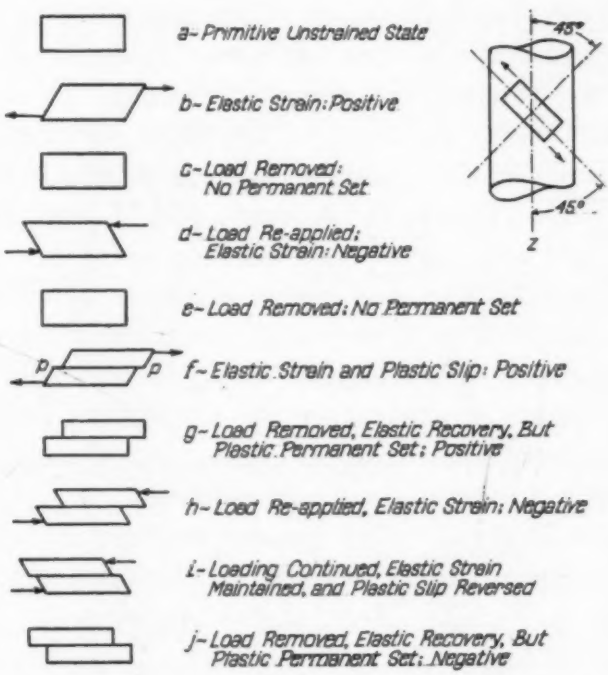
a- Primitive Unstrained State
b- Elastic Strain: Positive
c- Load Removed: No Permanent Set
d- Load Re-applied: Elastic Strain: Negative
e- Load Removed: No Permanent Set
P
P
f- Elastic Strain and Plastic Slip: Positive
g- Load Removed, Elastic Recovery, But Plastic Permanent Set: Positive
h- Load Re-applied, Elastic Strain: Negative
i- Loading Continued, Elastic Strain Maintained, and Plastic Slip Reversed
j- Load Removed, Elastic Recovery, But Plastic Permanent Set: Negative
45°
45°
Z

Fig. 2—Combinations of Elastic and Plastic Shear Strain. (Dalby)

Clearly, some combination of elastic with plastic strain must prevail during the cycle of loading and unloading a crystal in the general process of plastic deformation. W. E. Dalby (Strength and Structure of Steel and Other Metals, Longmans, 1923, p. 154) uses the simple diagram shown in Fig. 2 to explain his push and pull diagrams obtained with a sensitive optical recorder. These sketches represent the action of shearing couples resolved from the axial stress, as shown at Z, on a crystal block. From a to e are shown the effects within the elastic range as a positive elastic shear strain accompanying the pull, a return to the primitive state on removing the load, a negative elastic shear strain during the ensuing push and finally a return to the unstrained state without permanent set

on removing the load. The group of sketches f, g, h, i, j, representing deformations produced when the forces increase to values capable of producing slip along the gliding planes, is described as follows: "The forces first produce elastic deformation like b, and then a slip along a gliding plane pp as indicated in f. Removal of the forces relieves the elastic strain but leaves the parts of the crystal in their displaced positions as indicated in g. Reversal of force produces first an imperfectly elastic deformation h and slip of opposite sign. Removal of the load again relieves the elastic strain but leaves the layers in their displaced positions. The combination of elastic deformation with plastic slip thus explains the shape of the diagrams ....and also the torque-twist diagram". In all of this it is quite evident that no careful appraisal of the atom positions is taken and no picture is given of the shear strengthening which occurs when a succession of plastic strains is imposed upon the specimen. It may be recalled that Dalby gave very fine examples of the hysteresis loops which generally rise to a higher stress level when the load is removed and reapplied in a series of tests. In this perplexity he adopts the hypothesis that "relative sliding along a slip plane breaks down the crystalline structure, in the immediate neighborhood of the glide, into amorphous material" and remarks that experimental data on the many points at issue are wanting.

Perhaps the Dalby sketches require no further amplification as his general conclusion can be derived from sketches in which atom sites appear, as in Fig. 3. Here, atoms are supposed to be located at the corners of the parallelograms shown. For simplicity the unstrained cells are rectangular and the stress axis A1 is perpendicular to the slip planes. No resolved shear stress would result from this arrangement but subsequent geometrical steps are valid and the conditions of strain and rotation are more easily seen in this simplified representation. Elastic shear strain is shown in the second sketch and in order to maintain a symmetrical condition the axis must now occupy the position A2. If the axis is maintained in the normal vertical position the cells are seen to be rotated through the appropriate angle. This is the normal process of shear and rotation as seen in the model now exhibited. In the case of an elastic shear as shown, every cell participates in the shearing deformation, while in the further case of slip, as depicted by Dalby, the upper and lower halves move in the aggregate one step or identity period against one another necessitating a further change in position of the axis to A3

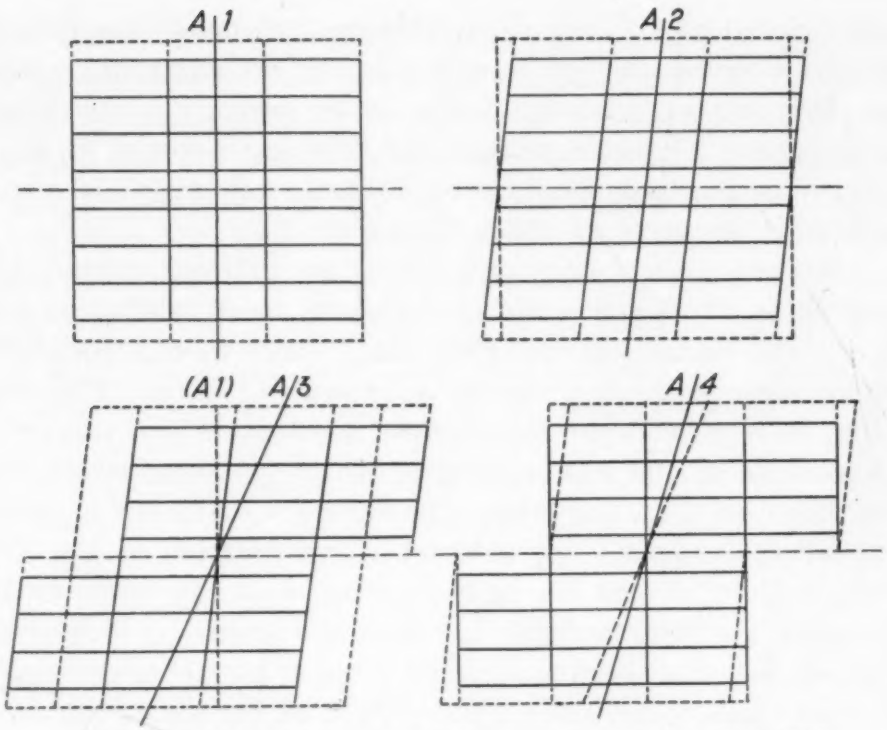


Fig. 3—Hypothetical Elastic and Plastic Shear and Axis Shift Without Strain Hardening.

just as if the final shear had been equally distributed among all of the cells. The atoms match at the inner surfaces of slip but the outer boundaries are now stepped. The axis must bisect the upper and lower extremities of the figure. Obviously, under the homogeneous condition shown the elastic shear in the entire structure can be removed by reversed shear and rotation when the load is released and this carries the axis from its dotted position to the position A4 in the last sketch.

This simple picture fails to satisfy our need for a configuration in which the essence of strain hardening can be found and it is entirely arbitrary in representing a localized slip through a vast potential barrier without regard for equilibrium with the adjacent lightly strained spacings. With regard to the latter deficiency, modern physical opinion has leaned strongly towards acceptance of lattice deficiencies or faulted structures as the cause of diminished resistance to slip in localized regions. This and an alternative premise of slip by deflection into a hypothetical path of reduced potential will be discussed later on.

The former deficiency may be overcome in some degree by postulating a condition of increased strain in the central spacing due

to its reduced area (after slip). Under such conditions the normal process of decreasing shear and rotation on unloading could not take place uniformly, as the central, more severely strained, spacing would require a greater rotation for complete removal of its shear strain. The resulting condition of internal strain might be visualized as the ultimate cause of strain hardening.

Certain considerations arising from the probable relationship between shear stress and strain as the atoms move relative to one another in the process of slip give added force to this possibility of variable shear strain in a plastically deformed crystal. The diagram of Fig. 4a represents the conventional assumption that this relationship is expressed by a sine curve in which the shear stress, at first proportional to the shear strain (Hooke's law), reaches a maximum value when the linear displacement is one quarter of the identity period, falls to zero at the halfway position (C/2) when all atoms of a plane are symmetrically between two atoms of a neighboring plane, reaches a maximum negative value at the three quarter point and finally falls to zero at the completion of the shear. E. Orowan (E. Orowan, Proceedings of the Physical Society. Report of a Conference on Internal Strains in Solids, Vol. 52, Part 1, 1940, p. 12) has used a mathematical expression of this relationship (Stress $\simeq$ $\text{Stress}_{\text{max.}} \cdot \frac{2\pi}{d} x$, for small strains) equated to the simple expression of Hooke's law (Stress = Modulus of Shear $\cdot \frac{x}{d}$) in a "simple and safe way to obtain an estimate of the maximum shear stress which the lattice can withstand."*

It is thus apparent that a given elastic shear stress may correspond to a small elastic shear, c/m, or a larger shear, c/n, approximately halfway through the identity period.

Fig. 4b shows a combination of such shears in a diagram similar to the one previously discussed (Fig. 3). Here, at 1, the balance between shear stresses in the upper homogeneous spacings is indicated by the dotted lines and short arrows and at 2 the balance between the large shear, ½ c/n, and the adjacent small shear, ½ c/m. On unloading such a structure the greatly different rotational tendencies of its inhomogeneous parts could not be realized and a condition of internal strain perhaps of complicated character could hardly be avoided.

*In these expressions, x represents the displacement and d, the distance between two adjacent lattice planes.

The conditions which might activate a partial slip as represented cannot be defined and this is merely an attempt to point out that conditions of equilibrium under stress leading to a probable complication of internal strain can, at least, be visualized in principle. Orowan's simplified estimation of the maximum shear stress required to force one layer of atoms over another in the established direction of slip is in harmony with previous conclusions of Polanyi

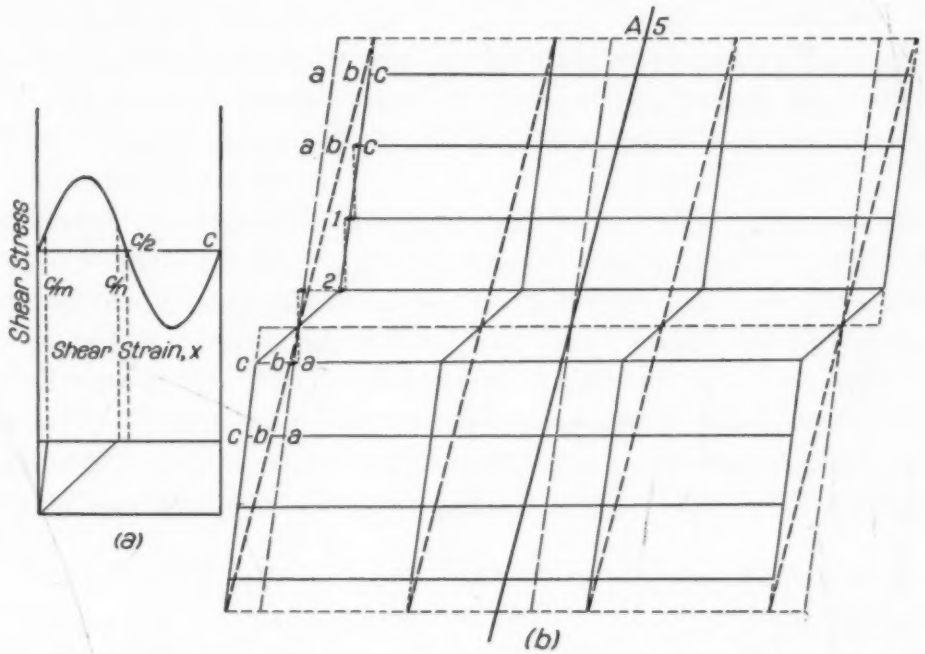


Fig. 4—Possibility of Variable Shear Strain in Plastically Deformed Crystal.

and others (Cf. M. Polanyi and E. Schmid, Die Naturwissenschaften, Vol. 17, 1929, p. 301) that the numerical order of the lattice forces is estimated to be 100 or 1000 times the forces observed at experimentally determined yield points. With reference to the simple picture of slip given in Fig. 3, the "Kernel of the plasticity question" is now, as it was 14 years ago when Polyani and Schmid used this phrase, the question why these great lattice forces can be overcome locally at a so-called slip plane without a general requirement of comparable stress to a comparable value of strain in all spacings throughout the body of the crystal as would satisfy the ordinary concept of equilibrium.

There appear to be only two avenues of escape from this dilemma. One of these, as previously noted, is offered by the widely-held theory of propagation of dislocations, or structural flaws, which

has received much attention and since G. I. Taylor's presentation of 1934 (G. I. Taylor, Proceedings, Royal Society, A 145, 1934, p. 362) has existed in a precise mathematical form. The other is the obvious attempt to find weakened potential barriers by altering the path of slip according to some plan of oscillation which preserves in summation the experimentally observed slip direction. In the last part of this lecture something more will be said about this more or less unexplored and purely hypothetical approach to the problem.

## Modern Geometrical Correlations Between Extension, Change of Orientation, Shear Stress and Strain in the Operations of Slip and Twinning

Thoroughly satisfactory correlations between the experimentally accessible geometrical factors of slip and twinning are now available in the literature of crystal plasticity and an exhaustive treatment of this subject may be found in the Schmid and Boas text (E. Schmid and W. Boas, Kristallplastizität, Springer, Berlin, 1935). Thus, the extension at the axial position A3 of Fig. 3, which evidently corresponds to a lengthening of this axis from its original dotted position A1, is simply related to the change of angle between the axis and the slip plane (from $X_0$ to X) through the formula $\frac{l_1}{l_0} = \frac{\sin X_0}{\sin X}$. Here, the angle between the axis and the slip plane is the same as the angle between the axis and the slip direction, $\lambda$, but in the general case whatever the orientation $\frac{l_1}{l_0} = \frac{\sin X_0}{\sin X}$ or $= \frac{\sin \lambda_0}{\sin \lambda}$. The shear, a, which is the distance between the axes A1 and A3 at any point divided by the thickness of the shearing block at this point. is related to the change of orientation through the formula, $a = \frac{\cos \lambda}{\sin X} - \frac{\cos \lambda_0}{\sin X_0}$. Various expressions may be derived from these and a useful one expressing the relationship between the extension, the shear and the initial orientation of the crystal is

$$\frac{l_1}{l_0} = \sqrt{1 + 2a \sin X_0 \cos \lambda_0 + a^2 \sin^2 X_0}$$

It is of interest to note that the configuration of stepped blocks representing plastic shear, change of length and change of orientation defined in the above relationships could be produced by a series

of readjustments of the atoms previously brought into a condition of uniform elastic shear as shown at one stage, with enormous exaggeration in Fig. 4. Considering only the atoms at the left-hand boundary their initial positions, following a small elastic shear, are at the a points (only a few of them lettered). Continuation of the elastic shearing process to a critical conclusion, as suggested above, brings the atoms to the b points, and finally the readjustment, which may be termed a plastic shear, brings them to the c points (reduces the shear strain and completes the single stage of slip). It has not been possible to obtain direct experimental evidence defining the condition of strain at the central spacing joining the sheared blocks, which in Fig. 4 is different from that of the adjacent spacings and in Fig. 3 is the same as the adjacent strain. It is evident that any condition of strain in the central spacing relative to the general strain in the block spacings can be *drafted* by suitable variation in the number of block spacings and in the amount of plastic shear at the median plane. The condition shown in Fig. 4 has been drafted as a possible one from the standpoint of balanced shears and the same reasonable condition would hold if longer blocks with the same shear strain had been used so as to permit a plastic movement through approximately one and a half spacings instead of approximately half a spacing as shown.

Notwithstanding the speculative nature of these premises and the lack of a complete kinematical picture, I have found it impossible to dismiss the recurrent thought that plastic action takes place in some such manner as this and is essentially a transfer of elastic strain energy from the body of slip lamellae to the inner slip surfaces. Deformational strain markings alone seem to require discontinuities of this character.

The observations of Mark, Polanyi and Schmid (H. Mark, M. Polanyi and E. Schmid, Z. Physik, Vol. 12, 1922, p. 58) on Zinc and Taylor and Elam on Aluminum (G. I. Taylor and C. F. Elam, Proceedings, Royal Society, London, Vol. 102, 1923, p. 643 and do. Vol. 108, 1925, p. 28) have supplied a satisfactory basis for interpreting the plastic adjustment of metal crystals to the requirements of simple axial stressing. It is clear that slip starts on planes, of the family permitting such movement, which carry the highest resolved shear stress and that the experimentally observed directions of slip move towards the axis in tension tests, while slip planes move towards the surface of compression in compression tests. Such re-

orientation obviously brings new planes into action in the case of crystals possessing more than one eligible set of slip planes and the thoroughly definitive geometrical analysis by Taylor and Elam established the [112] direction as the orientational end point for double slipping in the extension of face-centered cubic crystals.

As in the previous discussion of extension by plastic shear, these considerations are of a purely geometrical nature and do not involve the condition of strain at plastically sheared inner surfaces or other details affecting strain hardening. Indeed, the movement of an operating slip direction towards the stress axis might be considered to occur in differentiated stages, together giving the desired resultant. Thus, there has always been doubt concerning the origin of so-called annealing twins in face-centered cubic metals. Belief in a theory of lattice destruction akin to amorphization affecting the slipping process would carry along an easy assumption that the minute nuclei of twins could form on recrystallization of the crystal debris quite as easily as untwinned crystallites of various orientations. On the more attractive assumption that all atoms after plastic deformation are held in fixed positions of crystallographic strain by forces susceptible to analysis, however great the complication of the mechanics involved, the nuclei of annealing twins could result from slip in a direction [112] inclined 30 degrees to the accepted slip direction [110]. On this basis, the slipping process would be visualized as a succession of steps 30 degrees to the right and left of the resultant, macroscopically observed, slip direction; a first step setting up the twinned configuration in the single spacing involved and an ensuing step returning the atoms to the untwinned configuration while completing a fully integrated [110] movement.

The essence of this situation may be seen in the simple diagram of Fig. 5 showing the projection or plan of two close-packed layers of atoms at the slip site, the first by full circles and the second by point location of atom centers. Movement along the arrows sloping upwards is into twinned position. A continued movement along the arrows pointed downwards completes the slip along the horizontal lines as if it had proceeded in orthodox manner. Obviously, at any slipping site, the movements shown might cease at either stage, producing in the one case twinned and in the other case untwinned spacings plus such residual elastic strain as may be inherent in the process.

A dozen years ago K. R. Van Horn and I (C. H. Mathewson

and K. R. Van Horn, Transactions, Institute of Metals Div., A.I.M.E., Vol. 89, 1930, p. 59) attempted to direct a shearing stress in single crystal specimens of copper so as to produce twinning, if possible, in substantial amount. No success was had in this undertaking because, if we adopt the present line of thought, the load had to be carried by the close-packed strings of atoms, or [110] fibers, and these swing in and out of twin position at the slip site as the slipping progresses between any pair of planes.

The reluctance of aluminum to form annealing twins has always introduced an element of difficulty into the problem of rationalizing strain-anneal phenomena in general. On the present basis, it is

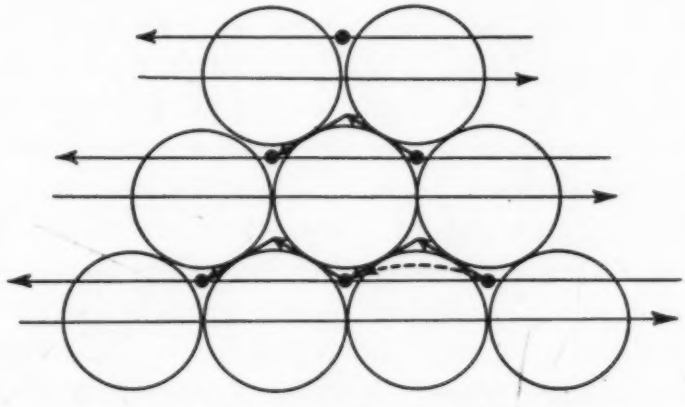

Fig. 5—Hypothetical Mechanical Twin Formation by Deviation of Slip from "Foothills" Into "'Valleys" of Close-Packed Face-Centered Cubic Structure.

merely necessary to assume that the twin position possesses a low order of stability in the aluminum crystal (on account of its electronic structure) and slip, which indeed may deviate from the [110] path, finds no natural end point close to the twin-position. The course of deviation designated as a curved (dotted) path in Fig. 5 is purely imaginary, although as will be pointed out in due course provides a qualitative explanation of orientations assumed in recrystallization after plastic strain. Something of this sort is required if atoms maintain space requirements at all consistent with their property of nesting into what seem to be more or less closely packed structures. Here, the [110] movement over the escarpment of the underlying atom, on a purely geometrical basis, calls for a dilation approximating 15 per cent, while the [112] movement with rigid spheres calls for only 6 per cent.

While the behavior of a single crystal under axial symmetrical

stressing could be satisfactorily analyzed in the geometrical sense by Taylor and Elam no such success has followed the many attempts to describe the behavior of the crystals in a conglomerate under any form of stressing. In particular the origin of observed textures has given rise to much controversy and Barrett and Levinson (C. S. Barrett and L. H. Levinson, Transactions, Institute of Metals Div., A.I.M.E., Vol. 137, 1940, p. 112) have made it clear that assumptions made by previous authors concerning the slip systems involved have been too greatly simplified. While there is no time for an adequate review of this exhaustive subject, a few points of interest are as follows:

Wever and Schmid (F. Wever and W. E. Schmid, Z. Metallkunde, Vol. 22, 1930, p. 133) viewing the constraint imposed on a crystal by its neighbors as a bar to the free movement of its slip directions towards the stress axis assumed that the movement in all cases was around an axis in the slip plane at right angles to the slip direction. After a certain amount of slip and rotation of the system carrying the highest resolved shear stress a second system came into play and the resultant movement due to this double slip in every crystal caused [111] directions in the several crystals to migrate towards the stress axis, thus simulating the major texture observed in face-centered cubic wires. It failed to reveal the [100] position also found in drawn face-centered cubic metals but gave the usual compression texture by an appropriate modification of the mechanism. A principal difficulty in accepting this plan of plastic deformation is the doubt that crystals could maintain their contact or fit after such disassociated movements without the development in them of elastic strains sufficient to bring other slip systems into operation and on general grounds one is inclined to agree with Boas and Schmid (W. Boas and E. Schmid, Z. Techn. Physik, Vol. 12, 1931, p. 71) that the operation of at least three slip systems would be required to permit the various changes of configuration necessary to maintain atomic contact of the irregularly shaped grains during their simultaneous deformation. These authors discard Polyani's suggestion that all slip systems of the appropriate family operate in favor of a restriction to the three systems carrying the highest resolved shear stress. Analysis of the problem on this basis leads to the anticipated experimentally observed textures of drawn and compressed cubic metals, as well as an evaluation of the principal rolling texture as a combination of compression with extension.

It seems apparent that there are a number of devices more or less competent to give a certain account of the principal textures observed in the usual processes of plastic deformation, but none of them can rationalize the more subtle differences which may be exhibited by different metals of the same crystal structure; e.g., rolling textures of aluminum, silver and alpha brass are similar but not identical while the texture of copper differs greatly from the others.

Taylor in the May lecture of 1938 before the Institute of Metals, London (G. I. Taylor, Journal, Institute of Metals, Vol. 62, 1938, p. 307) introduced a note of precision into current thought on

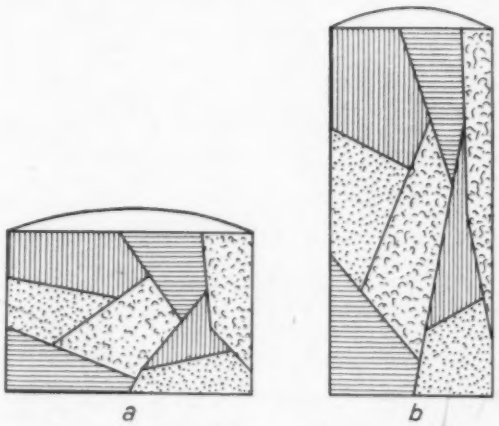


Fig. 6—Crystal Aggregate: *a*, Unstrained; *b*, After 125 Per Cent Extension. (Taylor)

the problem of the origin of textures by submitting mathematical evidence to the effect that complex slipping involving the action of five of the eligible slip systems in a crystal is necessary in order that the crystal may be perfectly plastic in the sense of accepting any strain whatever that may be forced upon it by an external agency. These five systems are the ones for which the work of deformation is least. The Taylor theory contains a prerequisite of homogeneous strain, as represented by his sketches, shown here as Fig 6; a, unstrained, and b, after an extension of 125 per cent. He writes: "The diagrams, which are drawn to scale, show on the left an imaginary section of a coarse-grained round bar, on the right the same bar with the same grains when extended to 2¼ times its initial length". Each grain suffers exactly the same strain as the surrounding material in bulk and this is the condition visualized by Taylor in the photomicrograph of a cross section of a drawn wire.

Barrett and Levenson (C. S. Barrett and L. H. Levenson, Trans-

actions, Iron & Steel Div., A.I.M.E., Vol. 135, 1939, p. 327) in a very elaborate experimental study of iron wires both in single and polycrystalline form have shown that the deformation is in no sense homogeneous but develops a special type of grain fragmentation into bands of varying orientations. Similar studies in compression tests on iron (C. S. Barrett, Transactions, Iron & Steel Div., A.I.M.E., Vol. 135, 1939, p. 296) and on aluminum (C. S. Barrett and L. H. Levenson, Transactions, Institute of Metals Div., A.I.M.E., Vol. 137, 1940, p. 112) and in cold rolling of copper (C. S. Barrett and F. W. Steadman, Transactions, Institute of Metals Div., A.I.M.E., Vol. 147, 1942, p. 57) have furnished a rich literature of detail comprising microstructural and X-ray studies of crystal break-up during plastic deformation.

Every brass metallurgist is familiar with the irregular, often wavy, displacement of the initially straight-sided twin bands of annealed brass when the metal is rolled or drawn. If twins of this character had been incorporated into Taylor's sketch, a, of Fig. 6, they would have drawn out into thinner straight-sided bands after the homogeneous deformation shown in his sketch, b. Instead of this, they commonly assume the irregular form shown prominently in the grain at the lower right of Fig. 7, which represents a common high brass wire drawn to a reduction of area of about 20 per cent after anneal to a grain size of about 0.150 mm. The first definitely observable microstructural effects of deformation in brass are these changes in the straight-sided twin bands.

Barrett in the 1940 paper finds that "about half of the grains in a carefully investigated polycrystalline compression specimen of aluminum rotate as predicted by the Taylor theory, about one third definitely do not and the rest are doubtful". He attributes this to nonuniform constraints on all sides of each grain affecting its strain. He further concludes that "owing to irregular inhomogeneous strain within the aggregate, no theory can succeed in predicting rotations of individual grains (i.e., the development of a texture) without taking into account an almost infinite number of variables. Attention must be directed instead towards a statistical theory that will explain the general trends and the dynamic equilibrium of the deformation texture".

It may be noted that an essential requirement of the Taylor theory to treat all metals alike, provided they exhibit the same slip systems on a purely geometrical basis, is relaxed if slip can be

Fig. 7—High Brass Wire Drawn to Reduction of 20 Per Cent After Annealing to a Grain Size of 0.15 mm.

analyzed as the outgrowth (by plastic rearrangement) of a prior elastic deformation. This is due to the variable elastic anisotropy of the different metals and constitutes a forceful argument for a theoretical approach to problems of crystal plasticity in which relationships between the elastic components of strain and the manifestation of plasticity are sought. Thus, the maximum and minimum shear moduli of aluminum are found in the [100] and [111] directions, respectively, and in the ratio 1 to 0.86 while the similar ratio for copper is 1 to 0.40 (Schmid and Boas, p. 202). This may constitute an ultimate basis for the pronounced difference in the rolling textures of these two face-centered cubic metals, or the capacity of the nearly isotropic aluminum to develop a simpler drawing texture [111] than the one produced ([111] plus [100]) by other face-centered cubic metals.

The source of the inhomogeneities of plastic deformation con-

tradicting the primary assumption of the Taylor theory may lie partly in the well known difficulty of obtaining a perfectly homogeneous elastic deformation* even in the simplest axial loading (Cf. for example, Cyril S. Smith, Proceedings, A.S.T.M., Vol. 40, 1940, p. 864, who with an especially constructed device was unable to obtain strain readings on two opposite sides of a specimen much better than 5 per cent apart), and partly in the circumstance that the atomic arrangement or state of strain at grain boundaries as well as the mere necessity for contact in bulk determines the choice of slip systems.

On the latter basis our general understanding of plasticity phenomena will be benefited by diversified studies of grain boundary effects. Various undertakings of this sort have been carried on in recent years by graduate students in the Hammond Laboratory. W. R. Hibbard (Yale dissertation 1942) prepared tension test pieces of copper containing a small number of crystals and investigated the behavior of each crystal with respect to strength, elongation, axis shift, and also amount of shear and resolved shear stress** insofar as the slip could be referred to definite planes and directions. The change of orientation was determined by X-rays and stereographic plots were made of changes in all crystals at each increment of strain. Numerous deviations from the theoretical great circle, expressing movement of the axis towards a slip direction, were found. For these cases the axis shift was measured on a great circle between the original and final orientations and no successful attempt was made to resolve anomalous movements quantitatively according to individual slip systems. One of the composite plots is shown in Fig. 8. Figures on the curves indicate the percentage elongation in the 2-inch gage length within which the different crystals were contained and the plots give properties in relation to the various grain boundaries as indicated.

Typical behaviors are as follows: Grain A was a large grain which, at a distance from B, occupied the entire cross section of the test piece. In this grain all axis movements conformed to single crystal behavior modified by slip interference due to the presence of the other grain. Curves for the 7 and 13 per cent elongations

*From which in the author's view the plastic deformation must arise.

**Calculated from the usual formulas:

$$a = \frac{\cos \lambda_1}{\sin X_1} - \frac{\cos \lambda_0}{\sin X_0} \text{ and } S = \frac{\text{load}}{\text{area}} \sin X \cos \lambda;$$

where X is the angle between axis and slip plane and $\lambda$ the angle between axis and slip direction.

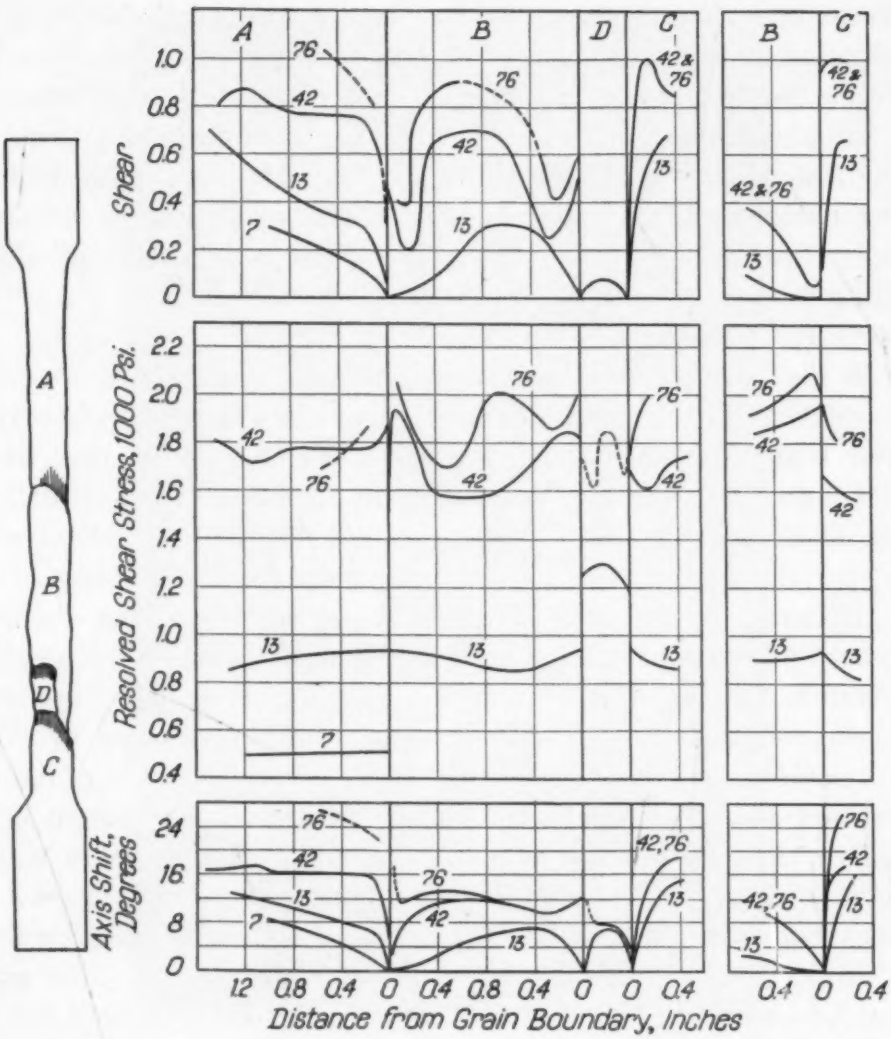


Fig. 8—Mechanical and Crystallographic Data Showing Changes Near Grain Boundaries of Coarse-Grained Tensile Test Specimen Shown at Left. Numbers on the Curves Indicate the Percentage Extension. (W. R. Hibbard, Jr.)

are similar, but in the latter case are displaced upwards. The slip interference is observed as a sharply decreasing axis shift close to the B-boundary covering about 2 degrees in the 7 per cent test and 8 degrees in the 13 per cent test. Further away from the boundary the interference persists as a gradient in axis shift, but in the 42 per cent test this gradient is overcome completely and the abrupt axis shift close to the boundary is followed by uniform behavior of the rest of the crystal. The resolved shear stress changes considerably near the boundary in the 42 per cent test and this effect of increased shear stress towards the boundary is noted as a characteristic of slip interference. Phenomena in grain B near A are quite

different and characteristic of so-called "forced slip" due to a predominating influence of the other grain or grains at the boundary. Here, in the 13 per cent test there was a complete interference with slip for a distance of 0.03 inch from the boundary and thereupon a gradient of axis shift extending beyond 0.8 inch. But with the higher elongations, typically the 42 per cent test, the axis shift rises abruptly towards the boundary in an area of active "forced" slip on a different system and in this area the resolved shear stress falls towards the boundary.

In the case of slip interference the resistance to deformation as measured by the resolved shear stress per degree axis shift is greater than normal in the boundary areas and in the case of the more common "forced slip" occurring in crystals normally small and under overall constraint from their neighbors the resolved shear stress per degree axis shift is less than normal in these areas.

Hibbard believes that he was able to rationalize the choice of secondary slip systems on the basis of the orientation of the operative slip system in the adjacent grains. Quoting from the "Summary and Discussion of Results" in his dissertation, "Since two neighboring crystals must deform so that their common surface remains intact, and since the orientation of the operative slip system determines the change of shape of a deforming grain, the easiest way to correlate the two factors was the operation of similarly oriented slip systems in both grains. This occurred in 12 of the 25 cases studied."

"In 4 other cases a condition approaching double slip in a single crystal was observed, i.e., major axes were similarly located but the slip direction in one grain was near the pole of the slip plane in the other. Under these conditions the two slip directions were approximately in the same plane as the stress axis."

"Since slip occurs in a slip direction of highest resolved shear stress and since stresses must be transmitted crystallographically, it seemed logical that the maximum force transmitted to a deforming grain would be along the slip direction of the transmitting grain, and would cause the operation of the slip system which had the greatest resolving power for this stress. The operative slip direction in the adjacent grain plotted as the stress axis in the Taylor and Elam stereographic circle (G. I. Taylor and C. F. Elam, Proceedings, Royal Society, London, Vol. 102A, 1923, p. 643; 108A 1925, p. 28) should determine the operative slip systems. Such an analysis was successful in 5 cases."

Fig. 9—Tension Specimen of Alpha Brass After Extension (9.3 Per Cent). (R. G. Treuting)

In all of this it seems evident to me that the principal slip in an embedded crystal occurs on one or two or perhaps three systems which alone produce observable markings, other systems contributing to a minor degree towards relieving elastic strain due to an otherwise imperfect fit at the boundaries.

R. G. Treuting (Yale Dissertation 1942) made a study chiefly of axis shift in coarse-grained tension test pieces of alpha brass and aluminum after the comparatively small nominal extensions over a 2-inch gage length of 9.3 per cent in the brass specimen and 9.7 and 20.0 per cent in two aluminum specimens.

The inhomogeneous nature of the deformation is at once evident in the appearance of the test pieces, as illustrated by Fig. 9, repre-

senting one side of the brass specimen. One or two sets of slip bands, rarely three, are seen variously concentrated in a given crystal and the irregular grain uplift leaves its record in the form of bands or regions of color contrast when the specimen is ground flat, repolished and etched. After this operation a certain residual etch-pattern of the supposedly effaceable slip bands can be seen in some of the crystals. This of course indicates a change of structure or orientation, as by twinning, at the slip sites. No trace of such an effect could be found in a Laue back-reflection pattern taken from a single crystal test piece showing closely spaced slip lines. The minimum distance between these lines was estimated to be 2000 atom diameters.* Assuming a slipping process yielding randomly the twinned or unchanged orientation at the inner surface of slip and an average distance between lines three or four times as great as this estimated minimum distance, the volume of twinned material would be in the range of concentration, 1/14000 of the volume, regarded by Barrett and Steadman (C. S. Barrett and F. W. Steadman, Transactions, Institute of Metals Div., A.I.M.E., Vol. 147, 1942, p. 57) as the limit of accuracy in their own unsuccessful X-ray search for twins in rolled copper. It thus appears that the question of mechanical twinning in copper and brass is not likely to be settled by direct X-ray observations.

Some of Treuting's principal conclusions follow:

"In the plastic deformation of coarse-grained polycrystalline alpha brass and aluminum by slight straining in tension, the most frequently observed rotation of the stress axis in the various individual crystallites is one about an axis lying in the operative slip plane normal to the operative slip direction. Other rotations at various angles to these, even 90 degrees, also occur. In addition, rotations in directions which would normally be associated with compression are frequent; in at least one such case it can be shown that a true compressive stress could be exerted on the grain in question by the effective application of a bending moment resulting from the orientation of the operative slip system in an adjacent grain."

"The greatest amount of axis shift from its original position occurred in the centers of grains. The boundary regions showed a multiplicity of slip systems operating complexly and frequently fragmentation as indicated by partial Debye-Scherrer rings, but less shear (axis shift)."

*See also R. G. Treuting and R. M. Brick. Trans. Inst. of Metals Div., A.I.M.E. Vol. 147, 1942, p. 128.

"Of the theories of plastic deformation of polycrystalline aggregates, that best fitting the present data is Taylor's, which gives axis rotations approximating those observed for perhaps half the grains. The failure of all present theories to take account of the stress inhomogeneities existing in the individual crystallites accounts for the discrepancies. It is possible that a theory of a statistical nature either cross-eliminating or integrating the stress irregularities would find success."

Other conclusions refer to the relation between the orientations of recrystallized grains and prior deformational characteristics. Since no positive correlations were secured details need not be given here.

It was suspected that this lack of correlation might be due to nucleation of the new crystals in material whose orientation was beyond the range of experimental detection by the methods available —presupposing that nucleation does take place without reorientation. It was further supposed that if nucleation does not take place without reorientation the successful theory of recrystallization is likely to be of a statistical nature based on the probability of occurrence of favorably arrayed groups of atoms, barring the development of new experimental techniques. Such a theory would wait upon the formulation of an adequate rationalization of the mechanism of plastic deformation of single crystals and of polycrystalline aggregates.

The matter of compressive rotations, indicating *compression* of part of a crystal in a test piece generally subjected to *extension,* demands some consideration. The case especially noted by Treuting concerns the behavior of crystals 17 and 18 in Fig. 10. It is stated that grain 17 was favorably oriented for slipping as compared with grain 18, and consequently yielded first by slip on the appropriate plane. In so doing it could exert a compressive force on part of grain 18 lying adjacent to it, as would a bending moment. The stress axis of this part of grain 18, originally located at 18, in Fig. 11 just above the [110] pole at I moved during deformation into this region as shown by the shaded area—a "compressive" rotation.

This assumes that the slip system under observation is BIV, the one normally possessing the maximum resolved shear stress in this triangular area. Treuting made no detailed micrographic study of the slip markings generally observed and indeed observations could be made only on the original surface, eliminating the possibility of identifying a slip plane by locating its traces in two planes.

Thus, while this is a compressive rotation for the most probable

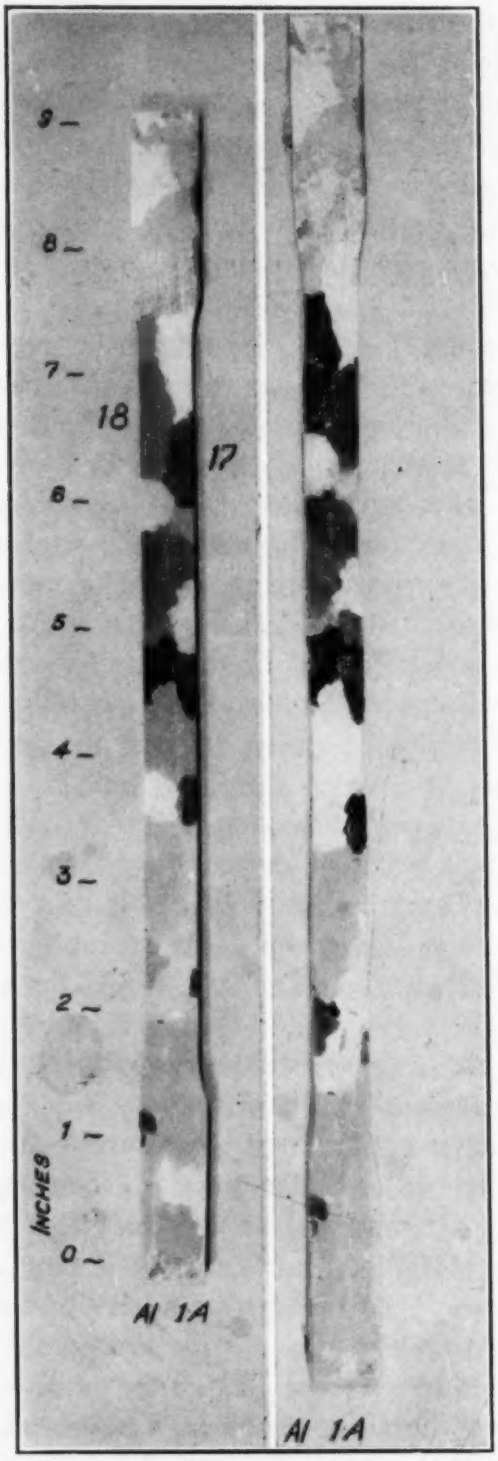


Fig. 10—Aluminum Test Piece Before (Left) and After Extension.

system, BIV, as shown by the directed arc, b, centered at the point marked ⊥ BIV (the axis in the slip plane B perpendicular to the

slip direction IV) carrying the axis, 18, *away* from the slip plane B (or towards its pole), as must happen in compression; a movement in this general direction would be *towards* slip plane A or slip plane C, and therefore an extension (the arc, centered at the point marked ⊥ AVI, follows very nearly the course of the arc, b, in the neighbor-

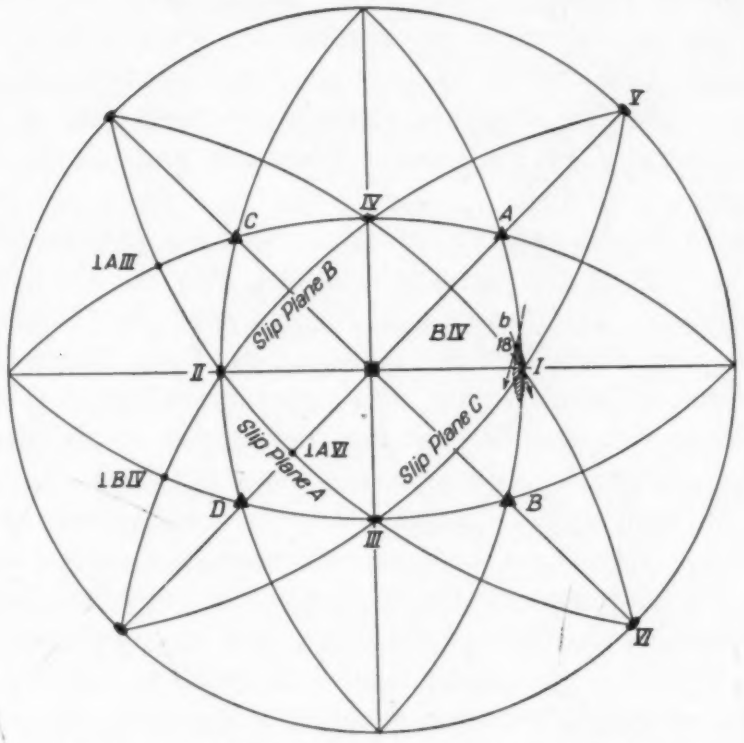


Fig. 11—Axis Shift in Crystal No. 18 (Schmid and Boas Nomenclature of Planes and Directions).

hood of axis 18 and the one centered at the point marked ⊥ AIII moves to the left as shown). Thus, if the A plane instead of the B plane were operating in forced slip, the axis shift observed would correspond to extension and not compression. Obviously, complications involving various slip planes might be encountered, slip without rotation might occur, and through it all we are left with considerable doubt as to whether crystals undergoing extension can actually substitute compression for extension in certain uniquely constrained locations.

## The Concept of Slip Interference

The period of nearly a quarter of a century between the discovery of slip bands by Ewing and Rosenhain and the clarification of the crystal geometry inherent in simple axial stressing of single

crystals by Mark, Polanyi and Schmid and Taylor and Elam was an active period of metallographic laboratory investigation establishing the microstructural appearance of the common metals and alloys in their various forms. Laboratory techniques of general preparation and etching were discovered and a widespread appreciation of the microstructural characteristics of cast and wrought or annealed and recrystallized metal gradually came about, with a certain specific utilization of these criteria in the commercial specification of metals and alloys. The fine structural detail of worked metal caused considerable difficulty in its proper resolution and above all in its interpretation.

In my own laboratory, studies of worked and annealed brass resulted in one of the first publications (C. H. Mathewson and Arthur Phillips, Transactions, A.I.M.E., Vol. 54, 1916, p. 608) exhibiting correlations between microstructure and degree of deformation or extent of annealing, although some of these relationships were understood and utilized in the laboratories of prominent brass and copper companies. Perhaps this paper urged the first insistent public claim that crystal "fragmentation" in some form constitutes the basis for significant property changes in cold-worked metal, although the microstructural evidence of far-reaching discontinuity within the grains must have been patent to many observers. In this paper the initiation of recrystallization at grain boundaries or other regions of supposed extreme fragmentation was recognized, the temperature-time dependence of the beginning of recrystallization on the amount of prior cold working was emphasized and the general correlation of grain size after anneal with temperature of anneal was attributed to a surface tension effect according to which each temperature would permit growth of grain to a certain equilibrium size. No attempt was made to set up a theory of constitution of the inner surfaces joining grain fragments. It was merely inferred that they must be the seat of the dislocation or strain lying at the root of the fundamental process of strain hardening.

A brilliant discussion of this paper by Zay Jeffries containing much original material chiefly on grain growth phenomena testified to his interest and activity in this field. He notes that his own study of the recrystallization of iron, mild steel and copper after varying degrees of cold work revealed the relationship indicated above between temperature of recrystallization and degree of cold work and that "in the course of these experiments" he "conceived practically

the same ideas regarding the reasons for recrystallization as those advanced in the article under discussion". Well aware that visible etch bands or lines of deformation do not occur in lightly worked structures, which however recrystallize at high temperatures, Jeffries observed, "it seems logical to take the stand that if differences in orientation can be seen within the same grain after cold work, it is proof that such differences exist; and that if differences cannot be seen by our ordinary microscopic methods, it is no proof that such differences do not exist". Evidently in some metals these inferred differences are seldom well developed micrographically and in the brass under discussion, cold working beyond some 20 per cent reduction in thickness is necessary to give good evidence of the change in the microstructure.* Relative to a supposed equilibrium grain size for each temperature, Jeffries had much evidence of great variability of grain sizes depending on many factors, such as rate of heating, condition with respect to grain size contrast or obstructions, amount of plastic strain, etc. He successfully rationalized the phenomena of so-called exaggerated grain growth, supplying a technique later utilized in the growing of single crystals for critical study in various areas of physical metallurgy, and in building up the conception of a "critical temperature for grain growth" or "germinative temperature" in Howe's suggested phraseology (H. M. Howe, Transactions, A.I.M.E., Vol. 61, 1916, p. 582) introduced a high degree of order into the general confusion of ideas afflicting the subject of recrystallization and grain growth.

In this day of routine application of X-rays to metallurgical problems, the following quotation from Jeffries' remarks in this very discussion offers a striking commentary on the prophetic realism of his imagination:

"It seemed to me (in 1916) that Bragg's X-ray spectrometer might be used advantageously in determining specific orientations, as well as in studying the changes in orientation during the recrystallization period. In correspondence conducted through James G. Biddle, Philadelphia, Mr. Bragg said that no such work had been attempted with the X-ray spectrometer but he thought it likely that positive results could be obtained. I have not carried the matter any further to date."

In the first two decades of the present century, along with the extensive development of microscopic metallography, there gradually

*Note (p. 60) that Treuting obtained ineffaceable bands after less than 10 per cent elongation in tension.

evolved, in this country at least, an interpretation of work hardening as slip interference due to the substitution of deviated paths through grain fragments for the continuous and uniform paths along slip planes through a virgin grain. This finally found expression at the end of the twenty-year "incubation" period in a broadly generalized "Slip Interference Theory of the Hardening of Metals" by Jeffries and Archer (Z. Jeffries and R. S. Archer, Chemical and Metallurgical Engineering, Vol. 24, 1921, p. 1057) which was conceived as much in relation to the newly discovered general cause of precipitation hardening by Merica and collaborators (P. D. Merica, R. G. Waltenberg and H. Scott, Transactions, A.I.M.E., Vol. 64, 1920, p. 41) as in relation to grain fragmentation by cold working. In essence, strain hardening is ascribed to "the slip interference resulting from the disregistry of slip planes at the boundaries of grain fragments"—and an additional cause was thought to be "the disorganized layer of atoms at self-stopping slip planes and the additional amorphous metal generated at the old grain boundaries".

The later work on resolved shear stresses in the different slip directions on the various slip planes gave ample evidence that merely a change of direction of slip from grain to grain or fragment to fragment could not possibly account for the great increase in resistance actually observed. Taylor (G. I. Taylor, General Discussion on Cohesion and Related Problems, Faraday Society, Nov. 1927) discussing this subject 6 years later writes, "The theory most commonly put forward as an explanation (for strain hardening) is that in a perfect crystal a very small shearing force parallel to a crystal plane will cause all the atoms in one plane to slide over the atoms in the neighboring parallel plane. The increased resistance to shear in an imperfect crystal is due to the fact that rows of atoms are held up at any imperfection in the crystal structure. This theory has many forms; the displaced material may, for instance, form keys in the crystal plane or, alternatively, the slipping may be held up at the boundaries between crystal fragments whose crystal axes are oriented at slightly different angles."

"As soon as the possibility of slipping parallel to a number of crystal planes is admitted, the whole theory falls to the ground. Taking the case of aluminum for instance, there are twelve possibilities of slipping, namely, four planes of slip and three directions on each plane. By combining a limited number of these it is possible for a crystal in any orientation to suffer a distortion identical with

that of the main body of the original single crystal when sheared parallel to one crystal plane of slip. The shearing force necessary to produce this distortion is of course least when the crystal axes of the fragment are parallel to those of the main body of the crystal but mathematical analysis shows that however the fragment is oriented the resistance to shear parallel to the plane of slip of the main body of the crystal cannot be greater than about twice the minimum value.

"It appears, therefore, that however favorably the fragments are oriented for increasing the resistance to shear, they cannot increase it to more than twice the resistance of the original single crystals, and if the actual distribution of crystal axes found from X-ray measurements is taken into account it is found that the increase in resistance to shear cannot amount to more than 2 or 3 per cent of the original resistance of the unbroken crystal." The same thought is expressed by Taylor in a later construction (G. I. Taylor, Proceedings, Royal Society, Vol. 145, 1934, p. 362), as follows: "Where the portions inside and outside a surface of misfit are supposed to be perfect crystals, but with crystal axes oriented in two different directions, easy gliding in the outer crystal would produce a definite strain (alteration of shape) in the surface of misfit while easy gliding in the inner crystal would produce a different strain. Thus the only types of strain which are possible as a result of easy gliding in both the inner and outer crystal are geometrically inconsistent at the boundary between them. If no other type of plastic strain is possible then the inner crystal completely lacks the portion of the outer crystal within which planes of easy glide cut any portion of the inner crystal. When the crystals are capable of slipping equally easily on several crystallographically similar planes, as for instance, when the crystals have cubic symmetry, this explanation of hardening due to cold work is no longer applicable, because by an appropriate combination of easy glides, the inner crystal can be given exactly the same strain as the outer one. Under these conditions therefore there would be no geometrical inconsistency between them."

This seems to dispose effectively of any simple postulate that changed orientation can greatly raise resistance to plastic shear. But, in the view of Jeffries and Archer there is the "disorganized layer of atoms at self stopping slip planes" and "additional amorphous metal at the old grain boundaries". We might admit the term amorphous metal in a historical sense and affirm in a modern view that these disorganizations can exist at inner surfaces or boundaries

only in balance with the main substance of the fragments and that the rise in stress necessary to propagate the slip through such crystallites must overcome the residual stress inherent in these residual strains. I have sought vainly for a simple picture accounting for all the important facts and have reached the conclusion that there is nothing simple about it, although a simple diagram such as

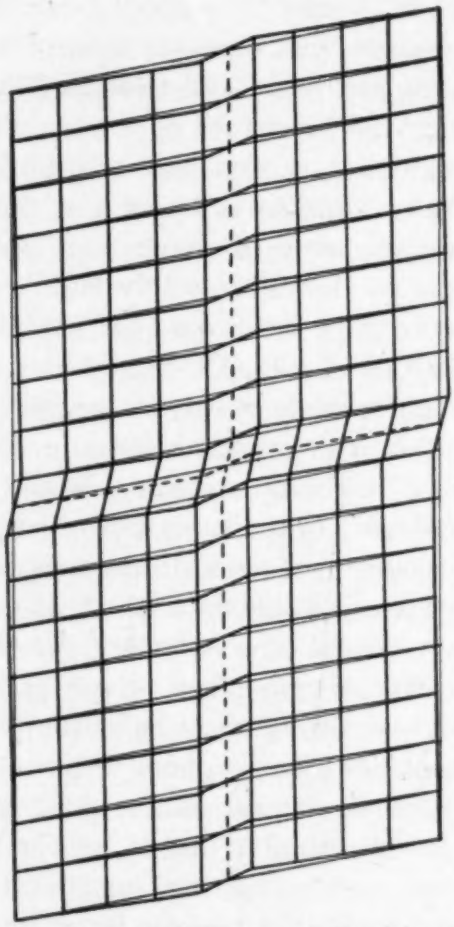

Fig. 12—Pattern of Combined Shears in a Hypothetical Lattice.

that of Fig. 4 may illustrate the essential idea of balance, with large strains at the boundary and small strains in the interior. Obviously, the rotated crystallites observed by many investigators do not take the form of continuous layers across the entire crystal as in this figure. Perhaps something akin to Fig. 12 in which, if it could be drafted correctly with regard for the actual lattice structure, shears would be balanced both longitudinally and transversely corresponding to fragmentation and boundary strain by shearing movements along two or more sets of planes.

In pursuing this subject further, Taylor in the 1927 Discussion held by the Faraday Society lays the foundation for the well known Taylor theory of fault propagation published seven years later in a completely quantitative form. Rejecting fragmentation as the source of strain hardening, he boldly argues that a perfect crystal is not weak, but strong, and that crystals as we know them contain regions in which "a high concentration of stress can occur so that very high values of the shear stress can be reached locally although the mean shear stress is small". These regions are flaws and their behavior is compared to the spreading and rotation of a crack when a shearing stress is applied parallel to its plane. Considering a crack as the limiting case of a very long ellipse "the stress concentrates at the ends of the crack and the direction of maximum shear stress in the region where it is greatest is that of the crack itself—so that it would extend in the same direction". Moreover, "throughout the whole of the two regions of stress concentration, i.e., at the two ends of the crack, the material is rotated about the transverse direction and the direction of rotation is everywhere the same, namely that in which rollers in the crack would rotate if they rubbed on the top and bottom of the crack. There is a concentration of rotation in the regions of concentration of stress."

Taylor now examines a carefully strained (compressed) crystal of aluminum with the X-ray spectrometer, adjusting it to the beam by rotation around an axis in the slip plane perpendicular to the slip direction, and finds reflections from the observed family of slip planes over a spread of some 10 or 12 degrees. Rotations around an axis in the slip plane parallel to the direction of slip give appreciable arcs of Debye rings which is consistent with the form of rotation postulated. This is in effect the form of rotation which would result if detached portions of the crystal acted as rollers between the slip planes. Taylor concludes that the rotation of an elastic material at the ends of a limited crack or area of slipping is therefore exactly what is observed by means of X-rays in a strained single crystal.

The cracks in the full development of the Taylor theory (to be discussed shortly) are faulted regions of crystal structure where atoms have been removed from the pattern.

"The increasing strength with increasing plastic strain is attributed to an increase in the number of faults or cracks. As the number of such faults increases the ratio of maximum stress, in a region of

stress concentration, to mean stress in the material would be expected to decrease. The mean stress necessary to cause a given maximum stress in a region of stress concentration must therefore increase as the number of faults per unit volume of the material increases."

I suppose a crude test of weakening by concentration of stress in a flaw may be had by pin-pricking the cellophane wrapper of your cigar which then can be pulled apart between the fingers, an almost impossible feat in the absence of the flaw; but I have not found it so clearly evident that the greater the number of pin-pricks the stronger the strip!

## The Taylor Theory of Fault Propagation

The concept of slip planes weakened by imperfect lattice development came prominently into view about 10 years ago following a great deal of attention to the general subject of mosaic structures and other imperfections including even the now discredited hypothesis of a thermodynamically stable mosaic pattern with regularly spaced weak planes (cf. in this connection Chapter V by W. G. Burgers of the Houwink volume on Elasticity, Plasticity and Structure of Matter, University Press, Cambridge, 1937; also M. J. Buerger, Zeitsch. Kristallog., Vol. 89, 1934, p. 242). Polanyi (Zeitschr. für Physik, Vol. 89, 1934, p. 660) sketches the condition shown here in Fig. 13 in which at the slip site within the inscribed circle eleven atoms above are opposite 10 atoms below. "If a lattice with such a missing atom site is given a shear which moves the atom rows 1/10 of a lattice period against one another, this homogeneous deformation will have the effect of maintaining unchanged the configuration of the zone of displacement, but of shifting its position through one lattice period". Polanyi summarizes the effect on shear strength as follows:

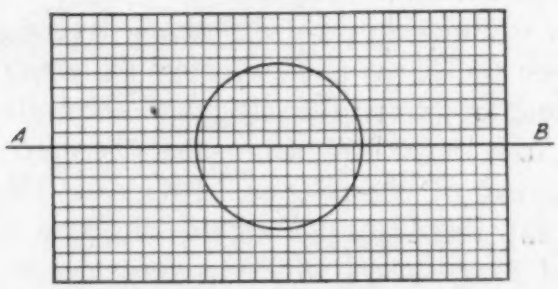


Fig. 13—Scheme of Lattice Displacement. (Polanyi)

"If a lattice displacement occurs on a glide plane, in which n atoms of one bank are opposite n + 1 atoms of the other, the resistance to shear along the glide plane will be weakened to approximately the nth part of the normal resistance". In order to account for the observed weakness of metal crystals (see p. 47) such regions of displacement must encompass a thousand atoms or so.

Orowan (E. Orowan, Zeitschr. für Physik, Vol. 89, 1934, p. 634) at about the same time proposed a mechanism of localized glide in which, under the influence of a shear stress, compression of the lattice on one side of the slip plane and extension on the other side brought about a slip or "jump" into the same general condition of dislocated fit between n and n + 1 atoms as the one just shown. In the accompanying Fig. 14 (taken from Houwink) eight atoms lie above and seven below in the left hand "positive" dislocation and seven lie above, with eight below in the right hand "negative" dislocation.

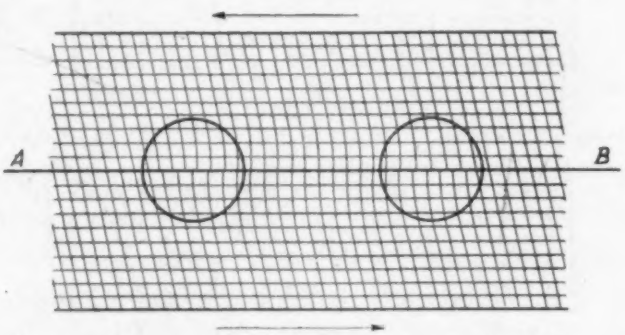


Fig. 14—Schematic Picture of a Local Glide "Jump": Formation of a *Positive* (at the Left) and a *Negative* (at the Right) Dislocation (After Orowan).

Taylor's paper (G. I. Taylor, Proceedings, Royal Society, Vol. 145A, 1934, p. 362 and 388) published the same year utilizes a very similar mechanism in that his earlier conception of cracks or flaws in the grosser sense gives way to a picture of faults on an atomic scale with localized slips causing a migration of atoms into the faulted areas, carrying them along until a boundary, again conceived to be a surface of misfit, stopped the process.

His diagrams, reproduced in Fig. 15, show, above, the movement of a "positive" dislocation from left to right as atoms feed in from right to left and, below, a similar, but reversed procedure carrying a "negative" dislocation out of the crystal at the left.

The mathematical treatment for coupled positive and negative dislocations was based upon a general theory of dislocations in an

elastic medium and gave first an expression for the shear stress necessary to cause migration of centers of dislocation, as follows:

$$S = c \mu \lambda \sqrt{N} / 2 \pi,$$

where c is a numerical factor of order of magnitude, unity; $\mu$, the coefficient of rigidity; $\lambda$, the identity period in the direction of slip, and N, the number of lines of dislocation per unit volume.

For shear strain, the expression, $s = N \lambda L$, was proposed. L is of especial significance in this analysis. It is the average distance between inner surfaces of misfit which stop the migration of dislocations.* This condition (permitting strain-hardening) is not represented in Fig. 15, where a movement of dislocations all the way to the outside surfaces of the crystal is shown. Such a condition in

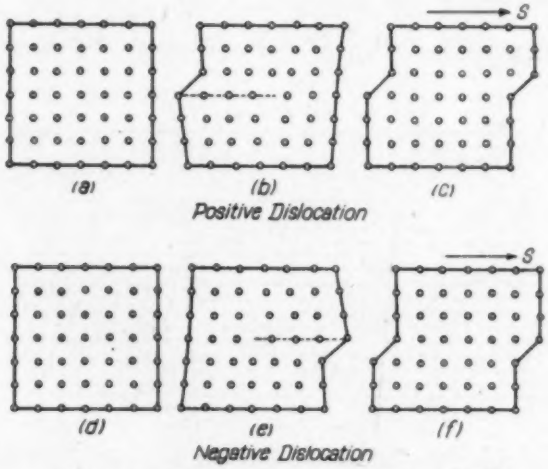


Fig. 15—Propagation of Positive and Negative Dislocations Through a Crystal. (Taylor)

Taylor's analysis would give critical shear stress values dependent upon the cross sectional area of the crystal.*

When the expressions for shear stress and strain, respectively, are combined, with elimination of N, there emerges Taylor's "remarkable" equation of parabolic form which seems to represent the commonly observed relationship between shear stress and strain in single crystals,

$$\frac{S}{\mu \sqrt{s}} = 0.16c \sqrt{\frac{\lambda}{L}}.$$

Taylor uses observed constant values of $\frac{S}{\sqrt{s}}$, obtained experimentally from tests on single crystals of copper, aluminum, gold and

*Cf. p. 389 of Taylor's 1934 paper.

iron, in connection with known values of c, $\lambda$, and $\mu$, in order to calculate the value of L, which he finds to be of the order of magnitude $10^{-4}$ cm. This he compared with the spacings of mosaic or other faults reported by other authors and finds satisfactory agreement.

The value of L is supposed to increase with temperature owing to decreasing "opacity" of the fault surfaces as thermal agitation of the atoms increases.

Objections to the Taylor theory so far expressed center around the use and meaning of this "mean free path" L, of the postulated dislocations. Thus, Burgers in the Houwink volume remarks in a precautionary vein that the calculated value of L depends rather considerably on the value of the constant, c, appearing in the final equation; that is, on the assumption made for the arrangement of the arrested dislocations.

Taylor writes, in this connection, in the original paper, "It will be seen that comparatively small variations in the arrangements of centres of dislocation produce very large changes in the value of K (viz., 0.16c). A crowding of positive centres of dislocation on one set of slip planes increases the ease with which negative centres can migrate along the intermediate planes". After introducing various assumptions as to the generation of dislocations and their effect on the shear stress and the strain, he writes, "In choosing a value to assume for K in order to compare the theory with observation we might take it that there are reasons for supposing that $K = 0.1$ is too low and $K = 0.3$ is too high, accordingly we may use $K = 0.2$ as the most probable value in the present very imperfect state of the theory. Calculations based on this value should at any rate give the correct order of magnitude for the strength of crystals".

Barrett (C. S. Barrett, Metals Technology, September 1943) in a very recent paper contributes interesting photomicrographs of copper, both annealed and compressed 75 per cent, monel metal after various treatments, and pearlite of different spacings, all of these obtained (after etching) with the electron microscope at various high magnifications (up to $\times$ 20,000). He finds blocks or domains which in annealed copper for example are rod shaped and about $3.10^{-4}$ cm. in diameter and in compressed copper, about $1.10^{-4}$ cm.* This is

*Barrett used an equation given by Bragg (W. L. Bragg, Nature, Vol. 149, 1942, p. 511) for calculating the strength of a crystal based on the reduction of strain energy in the block by slip at its boundary. Reasonable evaluations of the yield strength of annealed and compressed copper were obtained in this way.

pretty good agreement with Taylor's calculated value for L in copper ($2.7.10^{-4}$ cm.).

Accepting this value of L in the Taylor analysis, it is of course possible to use the formula, $s = N \lambda L$, to calculate N, the number of lines of dislocation per unit volume. Thus, Lennard Jones (J. E. Lennard-Jones, Proceedings, Physical Society, Vol. 52, 1940, p. 38) finds that "for a shear strain of the order of $10^{-1}$, N must be of the order of $10^{11}$ per $cm^2$. This implies that each small crystallite contains at any moment about 1000 such dislocations parallel to each of its principal axes. This is a very large number. It is nearly equal to the number of atoms along any one edge of the domain, and so we must conclude that each row of atoms on the surface of a crystallite is responsible for one of the dislocations in transit at any moment". Lennard-Jones therefore concludes that it seems desirable to consider other possible mechanisms of slip or modifications of the dislocation hypothesis.

The very advantage of a theory that rationalizes block slip in terms of weak planes between blocks becomes a disadvantage in seeking to rationalize twin-gliding which must affect all of the planes operating in conjunction to produce in macroscopic degree the simple shear, or modified simple shear, of mechanical twinning. If the gliding were confined to "weak" planes a thousand or so spacings apart, the twinned configuration could result only at the widely separated sites of slip and thus invisible twin lamellae would be interstratified with thick blocks of unchanged (or only slightly changed) orientation. Instead of this, wide, homogeneous, twin-lamellae are readily formed by straining zinc, tin, iron and some other metals. None of the advocates of the various "weak plane theories" have, to my knowledge, produced any helpful readjustment of this situation. M. J. Buerger (l.c. p. 70), on the other hand, writes with regard to the hypothetical secondary structure advanced by Zwicky, "In the case of twin-gliding, secondary structure supplies no mechanism at all. Twin gliding requires a mechanism consisting of shearing of sheets of atomic thickness, or rotation of complete secondary blocks. The latter mechanism is physically absurd and geometrically impossible on the basis of volume requirements. In other words there is no crystallographic possibility of producing a twin by shearing secondary sheets along week II-planes. If therefore it is admitted that shearing along planes of atomic dimensions can be produced by stresses causing plastic deformation (and there

is no way out of this) there remains no reason for a secondary structure as far as plastic deformation is concerned".

The same argument would appear to apply to any kind of "weak" planes. A considerable packet of planes must participate collectively in the considerable shearing displacement that is required for twin gliding. There might, indeed, be participation of planes across a mosaic misfit introducing a certain condition of heterogeneity into the twin lamella, but this would seem to be inconsistent with the general hypothesis of dislocated atomic bondings confining the slip to selected planes. If on the contrary slip can be viewed as an application of elastic strain energy from the block to a site of plastic displacement at the boundary, there is a good prospect of developing a complete kinematical picture of the process.

Measurements of internal friction in single crystals have emphasized the need for a structure in which plastic alteration can occur under the influence of the very small oscillating stresses used in these experiments. The idea of dislocations in the Taylor sense is advocated by Read (T. A. Read, Transactions, Institute of Metals Div., A.I.M.E., Vol. 143, 1941, p. 30) to explain his observations principally on copper and zinc. The dislocations are supposed to move back and forth in the crystal under the influence of the oscillating stress, assisted by random fluctuations of stress due to thermal motion of the atoms, thereby dissipating energy stored in the oscillations. Annealing decreases the number of dislocations and reduces internal friction, while plastic deformation increases the density of dislocations and, accordingly, the internal friction. Moreover, very small stresses, as low as 60 pounds per square inch in the case of copper or even 1 pound per square inch, contributed by the oscillating stresses themselves, in the case of zinc, change the structure of the metal in the sense of strain hardening with its associated increased internal friction.

This is good evidence for the presence of imperfections in metal crystals, which may be essentially the dislocations of Polanyi or Taylor, but there are unexplained irregularities in the damping behavior of different metals, and an essential requirement of the perfected Taylor theory that the movement of these dislocations must be arrested by a system of faults of a prescribed average spacing (L) was not considered in this application of the theory. Concerning the first of these reservations G. H. Found (Yale Dissertation 1943) in similar tests on copper, aluminum and 70/30 brass single crystals

observed the rise of internal friction in annealed copper after slight straining, but loads below the (mechanically observed) yield points of aluminum and brass generally decreased the internal friction* of the previously annealed crystals.

It is of course possible to depart from the Taylor theory by leaving out the assumption that new dislocations are formed and propagated so as to contribute their increments of shear strain as the deformation proceeds. Since the rising shear stress, S, is proportional to the square root of N and the shear strain to N itself there would then be no continuing parabolic relationship between S and s, but merely a small shear strain taking place at a low value of shear stress, affecting the number of dislocations originally contained in the crystal. Strain hardening as ordinarily observed would be due to some other cause and the movement of dislocations would be merely a preliminary small scale structural adjustment. On this basis, the increased internal friction of zinc and copper crystals after light stressing would be attributable to a specific incipient change in the condition of strain within the crystal, the decreased value after anneal to elimination of dislocations (faults) and the accompanying lattice strain, and the considerable increase after straining beyond the elastic limit to major strain discontinuities at block boundaries or some structural condition eventually found acceptable as the true cause of strain hardening.

## The Elastic Origin of Slip

The simple process shown in Fig. 4 of utilizing the elastic shear strain energy in the many spacings of a block to strain an intermediate spacing through the potential barrier opposing slip lacks the realization of unbalanced shears competent to force the rearrangement. Thus, in Fig. 16a every spacing of the elastically strained parallelogram (originally rectangular) is held in balance by the neighboring spacings. If a slip at the central spacing is carried one quarter of the distance through the identity period (one eighth on each side of the median plane) the position of maximum shear stress, m, of Fig. 16c (the usual diagram representing shear stress vs. strain in a single spacing) will be reached. There is now the impossible condition of the shear, $s_1$, somewhat less than the original shear, s,

*For example, in aluminum a decrease of 30 per cent after a stress application of about 500 pounds per square inch and in brass, a decrease of 25 per cent after stress of about 2000 pounds per square inch.

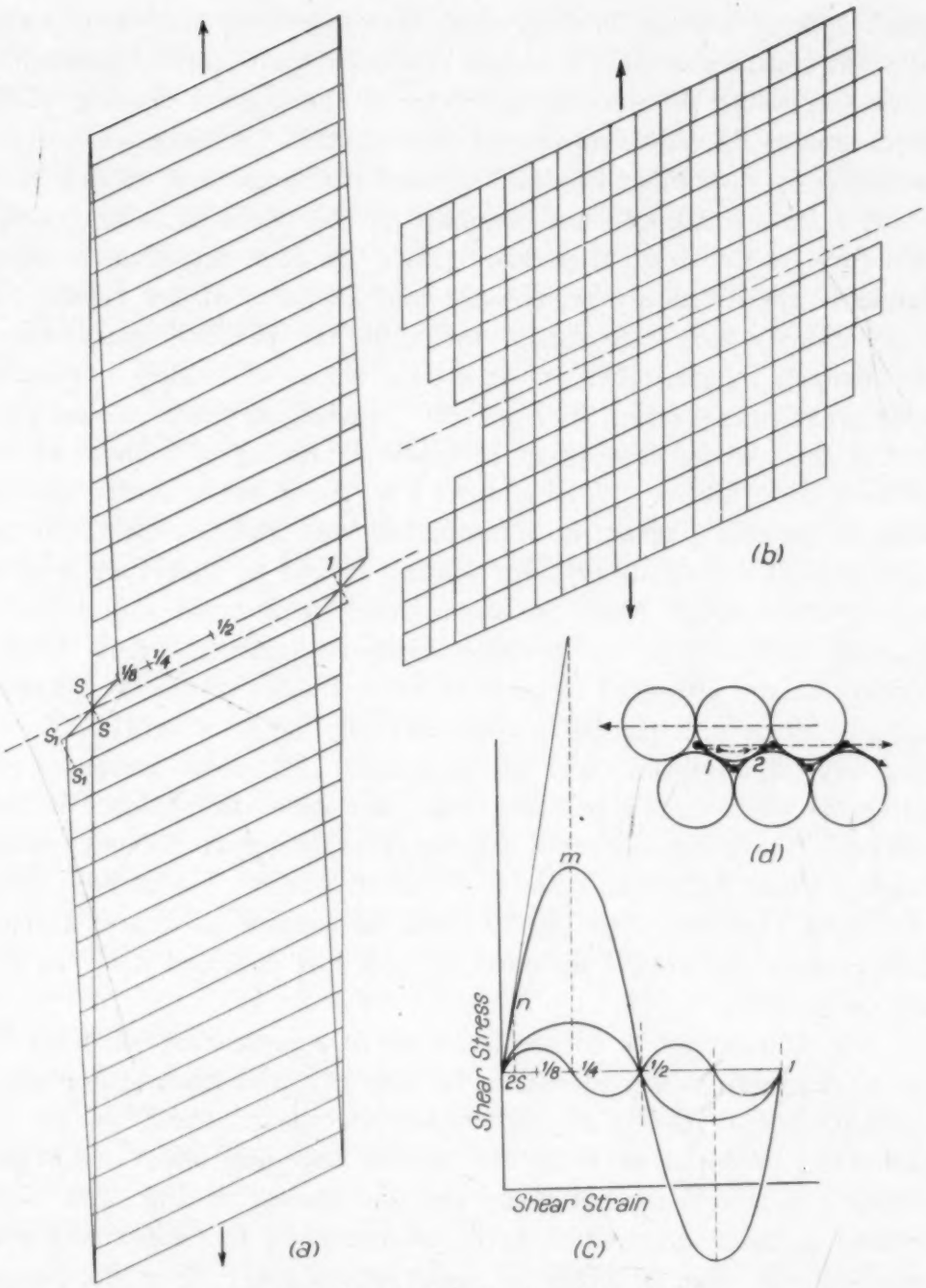


Fig. 16—Hypothetical Elastic Origin of Slip.

balancing the large shear, designated $\frac{1}{8}$, i.e., considering the sum of shears on both sides of the median plane, a shear stress somewhat below n of Fig. 16c, opposed to the maximum shear stress, m.

This is not a complete outline of the situation because in addition to the elastic shear strain shown, other components of strain (e.g., extension) must be encountered and the decreasing shear in the

block spacing during the suggested rearrangement may be expected to yield contraction as the atoms approach their normal unstrained positions, while the increasing shear in the central spacing yields expansion as the atoms move over one another. Whether or not this introduces a possibility of realizing any rearrangement of this character, certainly it could not originate in the perfectly homogeneous structure of the original parallelogram. A little reflection however makes it appear highly improbable that all parts of the crystal can carry exactly the same strain, owing to the practical certainty of dimensional irregularities on an atomic scale, as crudely illustrated with great exaggeration in Fig. 16b. Such a structure would yield first at the spacing possessing the smallest number of atoms and the greatest shear strain. Its location in Fig. 16b is at the dotted median line, but in this diagram no attempt has been made to show the assumed small variations in shear strain. There is, therefore, a compelling basis, apart from the assumption of internal faults, for a localized incidence of slip, perhaps continuing through many identity periods, before changing to another site. In this connection, Treuting and Brick (l.c. p. 60) in their examination of a lightly strained brass crystal, observed shear of the order of 700 atom diameters per active micrographically resolved slip plane and "the evidence is that once this shear has occurred further slip occurs at the next block spacing about 2000 atoms away". Barrett (l.c. p. 73) at high magnifications obtained with the electron microscope observed sharply differentiated lines as if an observed slip had confined itself to one pair of planes.

Fig. 16b cannot be construed to admit a premature incidence of slip at the small shear stress, n, of Fig. 16c constituting a minute fraction, say 1/1000th of the maximum shear stress, m, at the theoretical potential peak of the barrier opposing slip.* On the contrary if a structure such as the one shown in Fig. 16b were strained in accordance with the requirements of the uppermost sine curve of Fig. 16c, it might be expected to yield along the dotted path at a value of stress only a little below the calculated value for m in a homogeneously strained structure; which is of the general order of magnitude or the shear modulus, viz., $\simeq \frac{G}{2\pi}$, according to Orowan (l.c. p. 46).

*Parenthetically, it should be noted that in order to make these relationships visible in the various diagrams of Fig. 16 a greatly exaggerated value of n has to be taken. It should lie very close to the origin, as observed elastic shears are of the order of one hundredth or one thousandth instead of nearly one sixteenth of a spacing as shown here.

However, a mechanism of slip different from the one corresponding to the upper sine curve of Fig. 16c has already been suggested as a plausible basis for the nucleation of the twins which grow out of the confused pattern of deformational markings in most cold-worked face-centered cubic metals on annealing. This is a resolution of the macroscopic slip movement, according to the conventional plan of shear indicated by the long arrows in Fig. 16d, into movements 1 of twinning and 2 of return to the original structure.

It is assumed that a much lower stress requirement is associated with these movements except at the very early stage of the displacement. In Fig. 16c hypothetical stress-strain curves corresponding to these movements are projected from their true locations 30 degrees clockwise and 30 degrees counter-clockwise, respectively, into the plane containing the previously assumed stress-strain relationship during slip. These projected curves lie at the bottom in the left-hand half of Fig. 16c. While no detail near the origin can be shown on this scale, the underlying assumption is made that the close-packed strings of atoms are load carrying fibers which can be elastically strained in the rational slip directions, denoted by the long arrows of Fig. 16d, through a certain finite displacement before the stress requirement for movement of the atoms 30 degrees out of the line of highest stress concentration is realized. From this (yield) point onwards the stress requirement for these new movements is considered to be only a small fraction of the stress requirement for continuation of the original rectilinear movement over the walls of the low-potential valleys, and the result is a plastic shear, or jump, in the new direction.

If, owing to variations of electronic structure, the twin-position is not a stable point of 0-potential, some intermediate curve of shear stress vs. strain may be realized as shown. This is also a projected curve and corresponds to a hypothetical path of decreased resistance denoted by the curved arrows of Fig. 16d.

Inherent in this construction is the necessity for a different kind of rotation from the one accompanying the simple shear of the preceding diagrams (rotation around an axis in the slip plane perpendicular to the slip direction). As shown in Fig. 16d, atom strings pulling against one another in the directions of the long arrows separate laterally while moving forward and this exerts a complication of stress on the spacing which may be expected to yield not only by translation in some direction between the conventional slip and twin-

ning directions but also by rotation around its own polar axis. In other words the weakness of a spacing which is manifest in the commonly recognized process of slip may also manifest itself as a torsional weakness, apart from true shear.

There are two groups of experimental studies that lend support to this theory.

First, the work of Collins (J. A. Collins, Yale Dissertation, 1939), which came under my own observation in the Hammond Laboratory, while directed primarily to the study of rotations in the Taylor sense on a large number of aluminum crystals of different

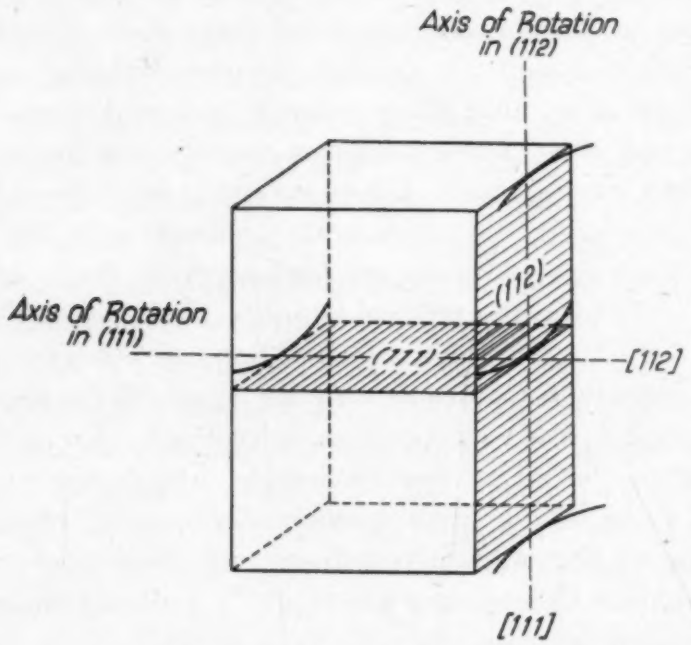


Fig. 17—Diagram of Possible Fundamental Rotations in Crystallites.

orientations,* i.e., the spread of diffraction spots from the slip plane corresponding to different settings of the crystal around an axis in the slip plane either normal or parallel to the slip direction, gave evidence of some other form of distortion. The situation is outlined in the simple sketch of Fig. 17. Here, the shading represents the slip direction and the observed change of orientation of the slip plane (111) from its horizontal position is indicated by an arc at either boundary described around the designated axis of rotation, [$\bar{1}$12].

*It would be idle to attempt a complete description of the strain in the "crystallites" of deformed single crystals and no detailed discussion has been introduced of various reported X-ray investigations which bear on this question. The difficulty in such undertakings is to find a simplification of conditions which will permit direct conclusions in the prescribed direction.

Change of orientation by rotation of the slip planes around their polar axis is similarly represented by an arc at the upper or lower right around the axis [111], with reference to observations on a vertical surface plane (112), normal to the slip plane. Of course some condition of fragmentation or crystallite formation by different amounts of rotation in different parts (blocks or lamellae) of the crystal must be envisaged in connection with this sketch.

A general summary of the observed reorientation of the slip plane in the "rotated" or strained crystallites is shown in Fig. 18

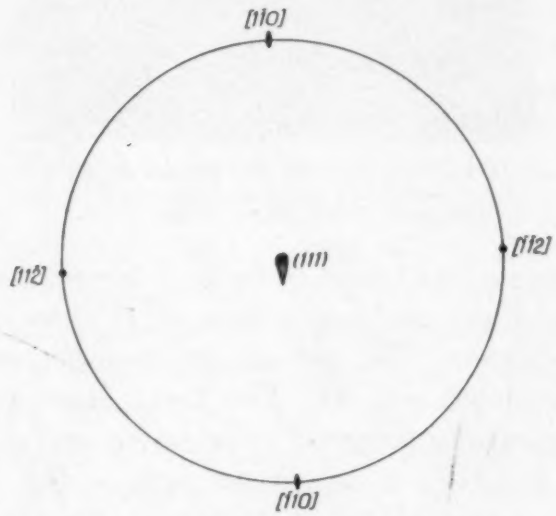


Fig. 18—Schematic Pole Figure for the (111) Plane Showing the Rotation of Crystallites with Reference to Normal Position of Slip Plane in a Strained Crystal.

as a schematic pole figure referred to the normal position of the slip plane in the strained crystal and reproduced from Collins' dissertation. The figure shows poles of the slip plane (111) spread principally in the direction of the [$\bar{1}$10] pole as would be caused by rotation about an axis [$\bar{1}\bar{1}$2] in the slip plane normal to the slip direction, together with a small spread of poles in lateral directions* Collins observes that this lateral spread would be caused by rotation about the slip direction [$\bar{1}$10] or might be of a more complicated nature. Obviously, if the slip direction were changed continuously by rotation of the slip plane about its own axis the (primary) rotation about an axis in the slip plane normal to the slip direction

*The major rotation is in the direction of the original unstrained orientation and in addition a small "negative" rotation in the opposite direction (a spread towards [1$\bar{1}$0] in Fig. 18) was observed. The major or "positive" rotation increased with the amount of shear but no relationship between the small "negative" or "lateral" rotations (maximum, 3°) and the amount of shear was apparent.

would produce a lateral spread of poles, as observed in these experiments.

A direct test of the hypothetical rotation around the vertical axis of Fig. 17 was made by G. H. Found in the Hammond Laboratory utilizing a specially selected single crystal of aluminum made by the strain-anneal technique. The straining process was expected to proceed in simplest form in this crystal because slip plane and direction were equally inclined to the axis (33.5-34 degrees). After

Fig. 19—Angular Distribution of Second Order Diffraction Maxima from (112) Plane of Aluminum Crystal After Slip.

straining, this angle was found to be 31.5 degrees, corresponding to an elongation of 7 per cent and a shear of 0.13 by operation of the appropriate slip system. The percentage elongation actually observed in a 2-inch gage length was 10. The X-ray beam was incident to a surface plane, carefully prepared by abrasion and etching, approximately parallel to $(\bar{1}\bar{1}2)$ shown at the right in Fig. 17, and normal to the axis of rotation [111] in the plane. Exposures were made with the angle of incidence of beam to specimen altered in steps of 1 degree in the vicinity of the normal angle for second order diffraction from the desired $(\bar{1}\bar{1}2)$ plane, using a copper target. Diffraction maxima were found at 66, 67, 68 and 69 degrees as shown in Fig. 19 indicating a rotation of 4 degrees of $(\bar{1}\bar{1}2)$ planes in the "crystallites" about an axis normal to both the slip plane and slip direction.

Finally, the "Taylor rotation" about an axis in the (111) plane normal to the slip direction was checked in this crystal by examining a surface plane cut parallel to the operative slip plane. Diffraction maxima over an angular spread of 4 degrees were also found in this test.

The other group of experimental results which in my view can be explained only in terms of some form of complex slipping, with an associated complexity of strain, concerns the origin of nuclei in recrystallization after plastic strain and the orientation of the new crystals. There is an abundant literature concerning textural conditions established in the various processes of cold working, which

must be carried far along to give recognizable effects of this sort, and find reflection in the associated recrystallization structure.

Although certain relationships, including often similarity between the "cold-worked" and "recrystallization" textures, have been noted, as if strained elements of the former gave rise to the crystals composing the latter, no good comparison between strained crystallites and recrystallized grains can be made because of the unknown combination of operative slip systems and the incapacity of X-ray techniques to reveal in their definition of the textural pattern the extreme orientations of minute amounts of the "fragmented" crystallites. The earliest studies of recrystallization (Cf., for example, Mathewson and Phillips (l.c. p. 64) made it clear that the new crystals grow out of the most severely strained regions of the matrix, as revealed by the etch-markings of severely deformed structures and there have been recent attempts to find the nuclei of recrystallized aluminum in the severe "local distortions" or crystallite rotations around an axis in the slip plane normal to the slip direction, following the analogy of "guide rollers" operating between the slip planes, associated with the Taylor theory. Barrett (C. S. Barrett, Transactions, Institute of Metals Div., A.I.M.E., Vol. 137, 1940, p. 128) reviews this situation with care and finds no clear predominance of the orientations that would be predicted by the Taylor theory in the texture of a single crystal of aluminum compressed about 70 per cent. "While fragments were found distributed throughout a range of 10 degrees from the mean orientation, the spread was not in the directions required by the theory".

In view of the uncertain complexity of the deformation when carried beyond its very early stages, it would seem most fruitful to search for the nuclei of recrystallization in axially strained single crystals oriented wholly within the range of operation of a single slip system. An important observation made by van Arkel and van Amstel (A. E. van Arkel and J. J. van Amstel, Z. Physik, Vol. 62, 1930, p. 43) that the growth of a crystal into its surroundings ceases if it is given even a slight amount of plastic strain seems to demonstrate that nuclei originating (by common observation) in the most severely strained parts of a crystal must have lost their strain before they started to grow. This has been interpreted in various ways. It may be imagined that they form spontaneously in the strained structure much as crystallization nuclei form in liquids. I prefer the interpretation that they are fragments or crystallites in a finite con-

dition of strain which at the effective temperature of recrystallization are unloaded from within and begin a new existence in their re-oriented state as strain-free, growing crystals.

It is not difficult to visualize fragmented areas of slip planes held in various stages of elastic shear strain between the macroscopic blocks with which we associate the term, block slip. While no complete picture of an internal unloading mechanism can be given, we know that the strain disappears on annealing and it may be pre-

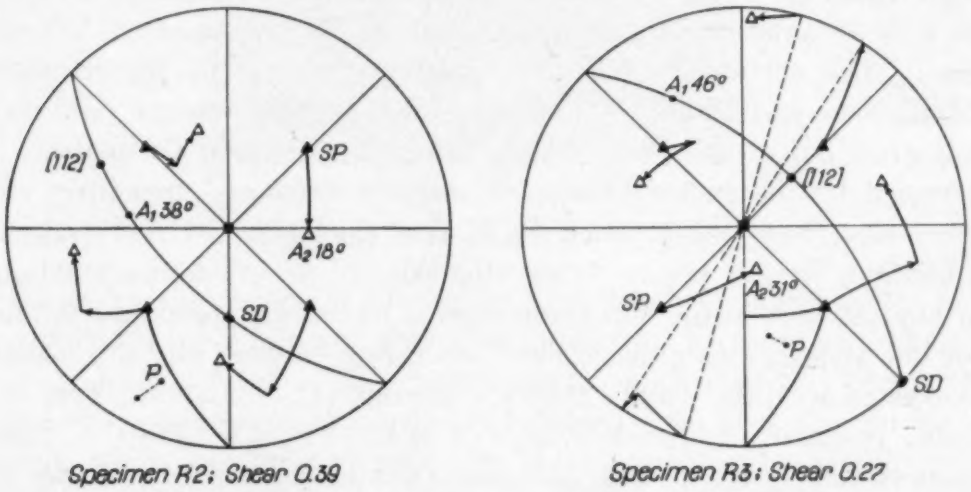


Fig. 20—Stereographic Projections with Constructions Giving Orientations of New Aluminum Crystals (Open Triangles) from Orientations of Original Strained Crystals (Black Triangles). SP Is Slip Plane; SD, Slip Direction; P, Pole of Specimen Axis; $A_1$, First Axis of Rotation and $A_2$, Second Axis of Rotation.

sumed that these strained crystallites tend to rotate as a simple mechanical model of elastically sheared blocks would on removing the tension load. If in the simplest atomic model the elastic shear had been less than halfway through an identity period the rotation would be towards the original unstrained configuration and if it had been more than halfway, so as to reverse the shearing force, the rotation would be away from the initial orientation.

A wide angular spread of orientations might result from such a process but the slip plane of reference in these nuclei would lie wholly in a zone determined by [112] the axis of rotation in the case of [110] slip in the generally accepted sense.

J. A. Collins (l.c. p. 80) has determined the orientations of two aluminum crystals obtained by annealing single crystal tension test pieces, designated R2 and R3, after straining to shears of 0.39 and 0.27, respectively, on the operating slip system. These are reproduced in Fig. 20. In neither instance could the orientation of the

new grains be related to that of the original crystal by any single rotation.

Obviously, a simple way to derive the orientation of one of these new crystals from that of its progenitor would be to find an axis of rotation in the original slip plane which would transfer this slip plane to its new location and then adjust the positions of all other rotated poles to their observed final positions by a second rotation, this time around the pole of the relocated slip plane. These operations are indicated by the arrows of Fig. 20.

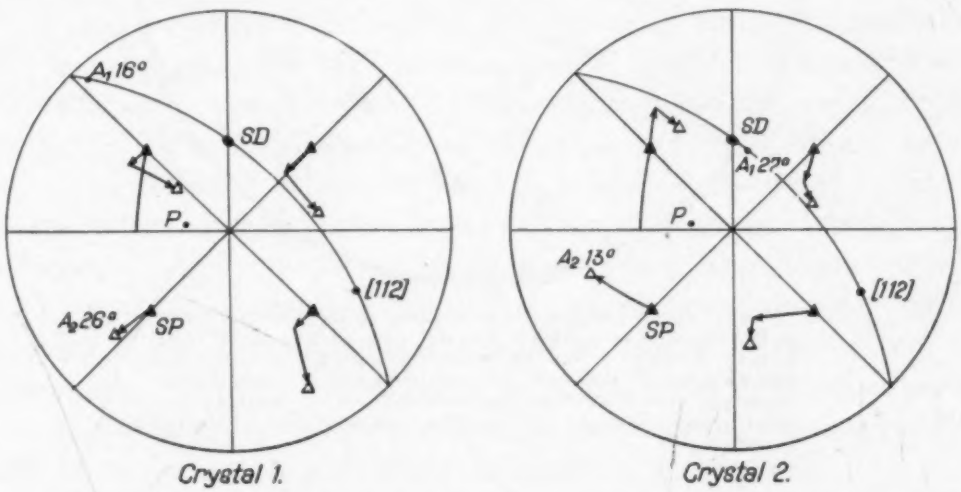


Fig. 21—Stereographic Projections with Constructions Giving Orientations of New Brass Crystals (Open Triangles) from Orientation of Original Strained Crystal (Black Triangles). SP Is Slip Plane; SD, Slip Direction; P, Specimen Axis; $A_1$, First Axis of Rotation and $A_2$, Second Axis of Rotation. Percentage Elongation of Strained Crystal, 3.75; Shear, 0.074.

A similar treatment of the two recrystallized grains obtained by Treuting (Yale Dissertation, 1942) from a single crystal of alpha brass annealed 15 hours at 850 degrees Cent. after straining in tension to an average shear over a 5-inch gage length of 0.074 is given in Fig. 21.

In spite of the generality of this process, which obviously can produce any desired reorientation, a physical basis is apparent in the assumption previously discussed that slip between blocks, actuated by elastic strain in the conventional [110] slip direction throughout the block spacings, can pursue a curved path of minimum resistance, resulting in complex strain, chiefly characterized by rotation around a variable axis in the slip plane combined with rotation around the pole of the slip plane. Various orientations arise from the different positions of strain held in equilibrium by the block structure and the

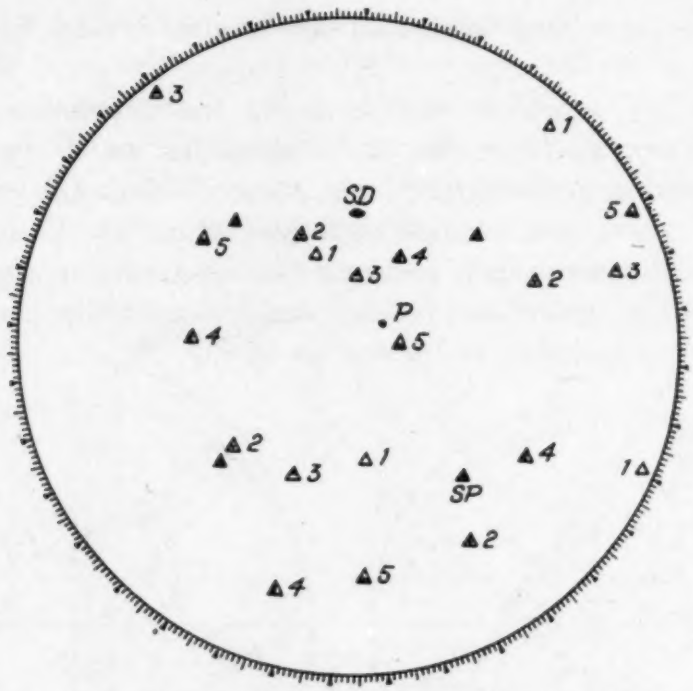


Fig. 22—Stereographic Projection of the Orientation of a Deformed Brass Single Crystal and of the Five New Grains Formed Upon Recrystallization. Solid Triangles Are Octahedral Poles of Original Strained Crystal; Open Markings Are Poles of New Crystals; P Represents the Stress Axis; SD and SP the Original Slip Direction and Plane.

consequent diversity of orientation assumed by the crystallites when their strain is released on annealing.

If this composite picture of plastic deformation and recrystallization seems extravagant in its nonconformity to the generally accepted idea of simple translation in crystallographically significant directions, it must also be admitted that some hitherto unannounced complexity of deformation is needed to clarify the devious relationship between recrystallized grains and the strained crystals from which they originate. In this latter connection, Barrett (l.c. p. 83) has given many examples of unpredictable orientations in the recrystallization of aluminum after extensive compression and I have reproduced in Fig. 22 from R. G. Treuting's dissertation, a projection combining the orientations of five recrystallized grains with the orientation of the original crystal after the comparatively small amount of strain which produced a tensile elongation of less than 10 per cent. The octahedral poles shown do not exhibit any easily specified characteristics of orientation. Perhaps the near-randomness of this distribution is influenced by the condition that the axis of the

crystal had reached a position corresponding to double slipping (which was actually observed on the specimen) and is so near the center of the projection that stress inhomogeneities might easily bring additional, closely adjacent systems into play.

Crystal No. 5 can be traced to twinning on the second slip plane, whose pole is the filled triangle in the upper left-hand quadrant, by performing the simple rotations corresponding to the assumed condition of strain in its original nucleus; viz., a rotation of about 10 degrees around an axis in the slip plane bringing this pole to the near-by position numbered 5; followed by the usual twin- rotations (180 degrees around the pole of the twinning plane) of the other octahedral poles, after their rotation around the first axis, and finally a rotation of some 20 degrees of these three "twinned" poles around the first. This brings all poles numbered 5 into the positions shown.

Crystal No. 3 is also twinned, but in this case with reference to the filled triangle in the lower left-hand quadrant which would not normally operate as a slip plane in stretching a single crystal with its axis in the designated position, P. The condition of double-slipping is not well enough understood in relation to the present interpretation of slip in its simplest form to permit any evaluation of this abnormality, which may indeed be due to some unknown condition in the crystal or unsymmetrical application of stress.

Crystals 1, 2 and 4 obviously may be derived from the original crystal by the double rotations previously described.

# THE TENSILE PROPERTIES OF ALLOYED FERRITES

By C. E. Lacy and M. Gensamer

*Abstract*

*This paper reports the results of a systematic study of the effects of alloying elements in solid solution on the strength and rate of strain hardening of ferrites of substantially constant grain size, as revealed by true stress-strain curves. The strengthening effect of an alloying element as a function of concentration may be represented by a single coefficient, and the strengthening effects of several elements in solution together are simply additive.*

IN a critical study of the factors affecting the properties of iron and steel, two main fields must be considered: the effect of composition and the effect of structure. Although it is possible to study the effect of structural variation in a single steel, the extension of the data obtained to steels of different composition is impossible without knowing the specific effect of alloying elements on the continuous or matrix phase of the structure under consideration. In steels, the matrix phase is usually ferrite. This present work was undertaken to determine the specific effect of alloying elements on the tensile properties of alloy iron ferrites.

Until the recent work of Austin (1)*, little comprehensive work had been done on the effect of alloying elements dissolved in ferrite. Mechanical property determinations had been made on individual iron binary systems, but it is difficult to use these data as a basis for comparison because varying methods of preparation result in alloys of different degrees of purity.

In the present study some 30 iron binary alloys were prepared with chromium, cobalt, vanadium, aluminum, nickel, molybdenum,

*The figures appearing in parentheses refer to the bibliography appended to this paper.

This paper was submitted by C. E. Lacy in partial fulfillment of the requirements for the degree of Doctor of Science in Metallurgical Engineering from Carnegie Institute of Technology, Pittsburgh.

A paper presented before the Twenty-fifth Annual Convention of the Society, held in Chicago, October 18 to 22, 1943. Of the authors, C. E. Lacy is associated with the International Nickel Co., formerly International Nickel Fellow at Carnegie Institute of Technology, and M. Gensamer is professor of metallurgical engineering, Carnegie Institute of Technology, Pittsburgh. Manuscript received June 23, 1943.

tungsten, silicon, titanium and beryllium as the added element. As far as possible alloys were made up to contain 1, 2 and 3 atomic per cent solute, but since these alloys were to be alpha ferrites, the limited solid solubility in some systems necessitated alloys of less than 3 atomic per cent. In addition, eleven ternary and quaternary alloys were prepared to study the combined effects of the alloying elements. Tensile property data were used in evaluating the alloys.

## Preparation of Alloys

Low carbon enameling sheet was used as the base material. The alloying elements were added as the electrolytic or unalloyed metal in most cases, but when these forms were not available, ferro alloys were used. Although the latter contained some impurities, the amount introduced into the iron was small, since the amount of the alloying element added was small. No attempt was made to produce ferrites of extreme purity; instead it was thought best to use a low metalloid base material of as nearly constant composition as possible.

The melts, weighing approximately 250 grams, were made under vacuum in a high frequency induction furnace. The alloying element itself was used as the deoxidizer when possible. When the element would not serve as a deoxidizer, carbon was added for this purpose. A special method of freezing, which involved slowly raising the high frequency coil around the crucible, virtually eliminated pipe and eliminated the necessity of discarding a large portion of the ingot. Alundum extraction thimbles were used as crucibles.

The resulting ingots, which were 1-inch diameter cylinders three inches long, were forged to ½-inch squares, homogenized for twelve hours at 975 degrees Cent. (1785 degrees Fahr.) and then cold-rolled to $\frac{5}{16}$-inch square rods. Two 3-inch lengths for tensile specimens were taken from the mid portion of these rods and samples for chemical analysis were taken from the two ends of the remaining portions adjacent to the section removed for the tensile specimens.

The tensile stock was then recrystallized by heating in a lead bath for five hours after preliminary tests had determined the temperature required to give a uniform grain structure for each alloy. It was thought that the recrystallization temperature might be used to control the grain size, but it was found that the grain

size was insensitive to time and recrystallization temperature and that is depended chiefly on the composition and amount of cold work.

The recrystallized tensile stock was machined into standard ¼-inch tensile specimens and then given a fifty hour treatment at 715 degrees Cent. (1320 degrees Fahr.) in wet hydrogen to reduce the aging characteristics prevalent in commercial low carbon irons. With sufficient treatment, it is possible to entirely remove the aging characteristics, but with ¼-inch specimens, the time necessary is rather long and the treatment results in grain coarsening. Therefore a standard time was set so as to prevent excessive grain growth during the treatment, but which was long enough to reduce aging very materially.

Chemical analysis was made only for the addition element since it was thought that the minor constituent content would not vary sufficiently from alloy to alloy to make the additional determinations worth while. One sample of the base material as melted under the same conditions was analyzed for the common impurities. Carbon and oxygen analyses were also run on several samples. In all cases carbon was below the one-hundredth per cent limit of accuracy of the analytical method while oxygen was below 0.025 per cent in the melts in which the addition alloy did not serve as a deoxidizer.

## Testing

Duplicate tensile tests were made on all alloys. On one of these, optical extensometer measurements were made to permit the determination of the yield strength. The stress to give 0.2 per cent permanent deformation was taken as the yield strength.

Simultaneous minimum diameter and load measurements were made on all specimens and the data plotted in the form of true average stress-true strain curves. By true strain, often called effective deformation or logarithmic strain, is meant the integral

$$\int \frac{dl}{l}, \text{ or } \log_e (l/l_o) \text{ or } \log_e(A_o/A).$$

These curves become straight beyond the maximum load in the tensile test. Their advantages have been discussed in the literature which now contains enough examples to make it unnecessary to reproduce typical curves in this paper.

Four quantities were determined from these curves: the slope of the straight line portion which is an index of the rate of work hardening, the stress intercept of the straight line at zero deformation, and the slope per unit stress at an effective deformation of 0 and 0.6. The slope per unit stress is obtained by dividing the

**Table I**

| Alloying Element | Weight Per Cent | Atomic Per Cent | Tensile Strength Psi. | Yield Strength Psi. | Red. of Area Per Cent | Elongation Per Cent | Slope of Stress-Strain Curve | Slope Per Unit Stress at 0 Strain | Slope Per Unit Stress at 0.6 Strain | Intercept of Stress-Strain Curve | Grain Size (A.S.T.M.) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Mn | 0.16 | 0.16 | 34800 | 8800 | 95 | 58 | 40450 | 1.126 | 0.671 | 35900 | 2–4 |
| Mn | 0.30 | 0.305 | 35700 | 12700 | 95 | 53 | 44200 | 1.249 | 0.710 | 35300 | |
| Mn | 0.37 | 0.38 | 35950 | 10200 | 93 | 57 | 36800 | 0.959 | 0.608 | 38300 | 4 |
| Mn | 0.62 | 0.63 | 37950 | 12000 | 92 | 56 | 42150 | 1.082 | 0.648 | 38900 | 4 |
| Cr | 0.83 | 0.89 | 33550 | 6000 | 91 | 60 | 38700 | 1.114 | 0.667 | 34850 | 3–4 |
| Cr | 1.67 | 1.79 | 34850 | 6200 | 90 | 57 | 38200 | 1.053 | 0.644 | 36350 | 3 |
| Cr | 2.53 | 2.71 | 36200 | 7500 | 90 | 56 | 39900 | 1.033 | 0.646 | 38000 | 2–4 |
| V | 0.80 | 0.875 | 34850 | 7300 | 93 | 57 | 41300 | 1.177 | 0.691 | 35100 | 5 |
| V | 1.63 | 1.78 | 39300 | 10300 | 91 | 54 | 43600 | 1.061 | 0.647 | 41150 | 5 |
| V | 2.75 | 3.00 | 42200 | 15200 | 89 | 51 | 45500 | 1.042 | 0.639 | 43850 | 6–7 |
| Al | 0.50 | 1.03 | 36650 | 9000 | 95 | 61 | 39350 | 1.032 | 0.637 | 38000 | 4 |
| Al | 1.00 | 2.05 | 40450 | 12500 | 91 | 57 | 43750 | 1.052 | 0.643 | 41650 | 5–6 |
| Al | 1.50 | 3.06 | 42150 | 14900 | 90 | 53 | 44600 | 1.012 | 0.629 | 44100 | 5 |
| Si | 0.43 | 0.85 | 42700 | 15400 | 82 | 52 | 47050 | 1.068 | 0.650 | 44000 | 6 |
| Si | 0.90 | 1.78 | 50150 | 20300 | 82 | 48 | 56650 | 1.096 | 0.664 | 51200 | 4 |
| Si | 1.40 | 2.74 | 56150 | 26000 | 92 | 51 | 58850 | 1.030 | 0.635 | 58150 | 6 |
| W | 1.44 | 0.44 | 37750 | 11300 | 78 | 50 | 40400 | 1.023 | 0.632 | 39450 | 4–5 |
| W | 3.05 | 0.946 | 43550 | 16900 | 86 | 52 | 48250 | 1.093 | 0.660 | 44150 | 6 |
| W | 3.99 | 1.25 | 46300 | 17900 | 86 | 51 | 50300 | 1.06 | 0.648 | 47400 | 6 |
| Ti | 0.60 | 0.70 | 43700 | 12700 | 88 | 50 | 48800 | 1.080 | 0.656 | 45100 | 4–5 |
| Ti | 1.14 | 1.32 | 50100 | 18800 | 86 | 49 | 54800 | 1.041 | 0.641 | 52600 | 4–5 |
| Ti | 1.83 | 2.12 | 57550 | 24000 | 77 | 43 | 61500 | 1.026 | 0.636 | 59950 | 6 |
| Mo | 1.69 | 0.99 | 42750 | 22000 | 90 | 52 | 48450 | 1.110 | 0.666 | 43650 | 6 |
| Mo | 3.48 | 2.05 | 48750 | 18200 | 88 | 50 | 54250 | 1.092 | 0.660 | 49600 | 5–6 |
| Ni | 1.03 | 0.98 | 39150 | 18700 | 72 | 47 | 42600 | 1.060 | 0.647 | 40350 | 6 |
| Ni | 3.12 | 2.97 | 46250 | ..... | 80 | 42 | 47850 | 0.968 | 0.611 | 49700 | 5 |
| Co | 1.04 | 0.99 | 34750 | 8900 | 96 | 55 | 41800 | 1.205 | 0.700 | 34750 | 3–4 |
| Co | 3.20 | 3.04 | 37200 | 13900 | 73 | 47 | 40100 | 1.033 | 0.637 | 38800 | 3–5 |
| Be | 0.26 | 1.58 | 59250 | 31000 | 82 | 44 | 55100 | 0.854 | 0.564 | 64650 | 3 |

slope by the stress required to give a certain effective deformation. In the first case, the slope would be divided by the zero intercept.

These four quantities together with the tensile strength, yield strength, reduction of area, elongation, and grain size values are given for all alloys in Tables I and II. All values except the yield strengths are the average of the two tests. The yield strength values are from a single test.

**Table II**

| Alloying Element | Weight Per Cent | Atomic Per Cent | Tensile Strength Psi. | Yield Strength Psi. | Red. of Area Per Cent | Elongation Per Cent | Slope of Stress-Strain Curve | Slope Per Unit Stress at 0.6 Strain | Slope Per Unit Stress at 0 Strain | Intercept of Stress-Strain Curve | Grain Size (A.S.T.M.) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Ni<br>Si | 1.02<br>0.49 | 0.97}<br>0.97} | 48550 | 24200 | 75 | 44 | 48050 | 0.928 | 0.595 | 51750 | 6 |
| Ni<br>Cr | 1.04<br>0.92 | 0.99}<br>0.99} | 39700 | 11200 | 90 | 52 | 43970 | 1.086 | 0.656 | 40600 | 4–5 |
| Si<br>Cr | 0.51<br>0.93 | 1.01}<br>0.99} | 43200 | 13600 | 94 | 53 | 45250 | 0.987 | 0.619 | 45850 | 3–5 |
| Ni<br>V | 1.08<br>0.94 | 1.03}<br>1.03} | 39450 | 15300 | 92 | 55 | 41250 | 0.991 | 0.622 | 41500 | 4–5 |
| Ni<br>V | 2.17<br>0.95 | 2.06}<br>1.04} | 45250 | 19300 | 91 | 51 | 49050 | 1.057 | 0.646 | 46400 | 4–5 |
| Ni<br>V | 3.15<br>0.93 | 3.00}<br>1.02} | 48150 | 25600 | 90 | 48 | 48400 | 0.958 | 0.608 | 50500 | 5 |
| Co<br>Cr | 1.10<br>0.97 | 1.04}<br>1.04} | 34400 | 7200 | 92 | 54 | 42050 | 1.220 | 0.704 | 34500 | 2–5 |
| Mo<br>Cr | 1.76<br>0.85 | 1.03}<br>0.92} | 42400 | 14100 | 88 | 55 | 47150 | 1.083 | 0.657 | 43500 | 5–6 |
| Si<br>Mn | 0.49<br>0.07 | 0.97}<br>0.07} | 43550 | 20500 | 94 | 52 | 46700 | 1.032 | 0.637 | 45300 | 3–5 |
| Ni<br>Cr<br>Si | 1.09<br>0.95<br>0.51 | 1.03}<br>1.01}<br>1.01} | 48600 | 24100 | 91 | 49 | 50400 | 0.999 | 0.625 | 50400 | 5 |
| Si<br>Al<br>V | 0.52<br>0.32<br>0.99 | 1.02}<br>0.66}<br>1.07} | 44400 | 16300 | 91 | 50 | 49650 | 1.087 | 0.658 | 45650 | 3 |
| Unalloyed Fe .... | | | 33900 | ..... | 71 | 48 | 36800 | 1.023 | 0.634 | 34900 | 3–5 |

Analysis of remelted unalloyed iron: Mn—0.005, Si—0.06, P—0.009, S—0.018, Cu—0.005.

## Tensile Strength

The tensile strength values are shown in Figs. 1 and 2 in which they are plotted against weight per cent alloying element and against atomic per cent alloying element respectively. In these curves the zero per cent value of the extrapolated chromium curve was used as the tensile strength value for unalloyed iron. The value actually obtained for unalloyed iron was 33,900 pounds per square inch, some 1600 pounds per square inch above the extrapolated point for chromium.

It might at first be supposed that this discrepancy is caused by a decrease in the hardness of iron through the addition of chromium; however, it is difficult to visualize a metallic solid solution in which the addition of foreign atoms would result in a loosening of the lattice and a consequent decrease in hardness and tensile strength. The more probable cause is the effect of

the minor constituents such as carbon, oxygen and nitrogen. Low and Gensamer (2) have shown that very small quantities of these elements have a pronounced effect on the aging and yield point characteristics of iron. It is also quite probable that they influence tensile strength and hardness even though only minute quantities

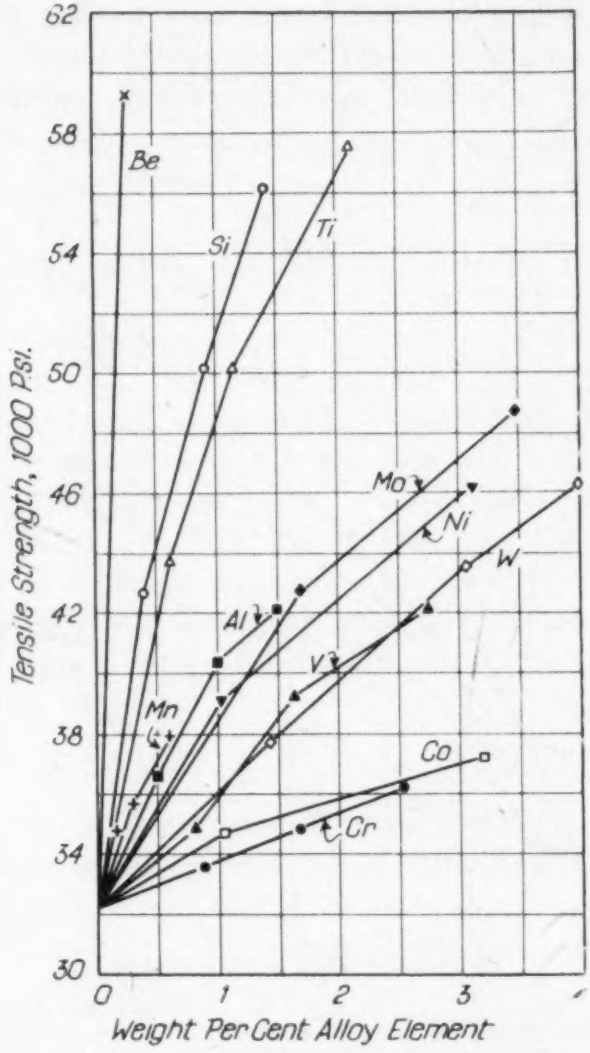


Fig. 1—Tensile Strength Versus Weight Per Cent of Alloying Element.

may be present. Thus the tensile strength of iron obtained from the extrapolated chromium curve might be lower than the measured value of iron because chromium is a more effective deoxidizer than carbon, which was used to deoxidize the iron. The tensile strength for iron obtained by extrapolation of the other alloy curves could lie a little above the extrapolated chromium point for the same reason.

Table III is a listing of the alloying elements that were studied arranged in the order of their capacity to strengthen ferrite, based on composition expressed in both weight per cent and atomic per cent. The most effective element, beryllium, heads both lists, and the least effective, chromium, is at the bottom of both lists. The order by weight per cent is the same as that given by Bain, except that nickel and molybdenum are interchanged; the difference between them is very little, especially at low concentrations.

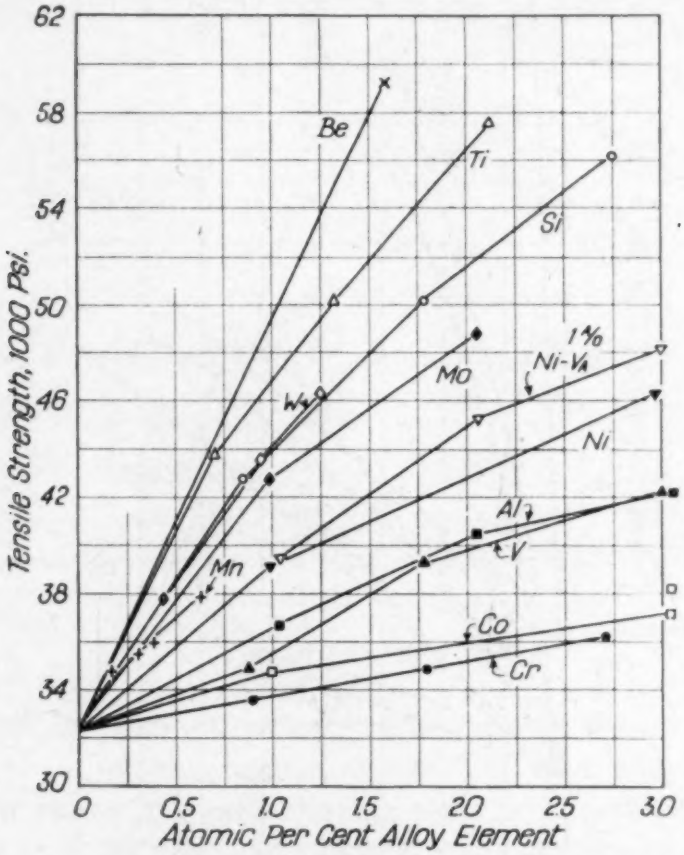


**Fig. 2—Tensile Strength Versus Atomic Per Cent of Alloying Element.**

An interesting observation in connection with the tensile strength-concentration relations is that they form a family of curves which are nth degree parabolas of the same degree. The curves for the several elements very nearly satisfy an equation of the form:

$$(TS) - (TS)_o = k\,(X)^n$$

in which $(TS)_o$ is the tensile strength of unalloyed iron and X is concentration. The n value is very nearly the same for all the

**Table III**
**Order of Effectiveness in Strengthening Ferrite**

| Order Based on Weight Per Cent | Order Based on Atomic Per Cent | Strengthening Coefficient for Tensile Strength | Solubility Atomic Per Cent |
|---|---|---|---|
| Beryllium | Beryllium | 19000 | .. |
| Silicon | Titanium | 14000 | 4 |
| Titanium | Tungsten | 11000 | 1 |
| Manganese | Silicon | 11000 | 26 (or 9?) |
| Aluminum | Molybdenum | 9600 | 2 |
| Molybdenum | Manganese | 7000 | 12 |
| Nickel | Nickel | 6100 | 19 |
| Vanadium | Aluminum | 4000 | 25 |
| Tungsten | Vanadium | 4000 | 32 |
| Cobalt | Cobalt | 1800 | 77 (?) |
| Chromium | Chromium | 1400 | 42 |

alloying elements studied. In logarithmic form, the above equation becomes:

$$\log\{(TS) - (TS)_o\} = \log k + n \log (X)$$

A plot of $\log\{(TS) - (TS)_o\}$ versus $\log (X)$ is given in Fig. 3, with X in atomic per cent. The parallelism of the lines indicates a constant n value of ¾. The value of k which is the intercept of the lines at the one atomic per cent ordinate may well be used as a quantitative index of the effect of an alloying element in strengthening iron. This value of k, called the strengthening coefficient, appears in the third column of Table III, the numbers referring to the elements listed in the second column. The value for beryllium, with only one point on the line, is, of course, questionable.

A number of factors may be used to explain the different hardening effects of the several elements. Rosenhain (9) suggested that the hardening effect should be inversely proportional to the solid solubility. Norbury (10) showed the hardening effect to be related to the difference in size of the solute and solvent atoms. Among those who have recently discussed this subject, Austin (1) mentioned low solubility of the solute, difference in crystal structure of the solute, and difference in atomic radius of the solute from that of iron as giving a greater increase in strength of the iron; Frye (3, 4, 5) in his work on copper and silver solid solutions showed a relationship between change in lattice parameter and increase in hardness; Brick (6) found that the difference in atomic volumes between copper and its solute element could be used to partially systematize the hardening effects (a greater atomic volume difference causing a greater increase in hardening) and

that copper solid solutions obey the generalization that solution hardening increases as the solid solubility decreases.

The main factor in the increase of hardness of a solid solution caused by the addition of a solute is undoubtedly the local distortion of the lattice. The greater the distortion or the less easily the solute atom can be accommodated in the solvent lattice,

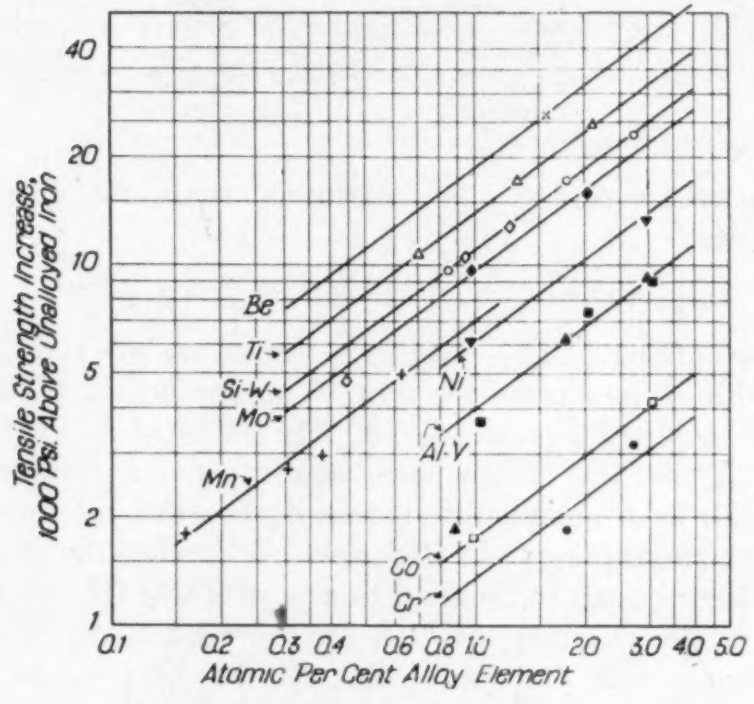


Fig. 3—The Increase in Tensile Strength Caused by the Alloying Element Versus Atomic Per Cent of Alloying Element, Plotted Logarithmically to Show that the Increase is a Power Function of the Concentration ($y = kx^n$) with the Same Value of n (0.75) for all the Alloying Elements Studied. The Intercept for Each Curve at One Atomic Per Cent (k) is the Strengthening Coefficient.

the greater will be the disturbing effect on the deformation process and the greater will be the effect on hardness. In analogous binary systems where the solute atoms being compared are quite similar and where solubility may be large, the overall change in lattice parameter is probably a good measure of the local distortion, and hence can be used as an indication of the hardening that can be expected. However, for widely different solutes this measure cannot be used. Perhaps the best measure of the distortion produced by the introduction of a solute into a solid solution can be obtained from the binary phase diagram plotted on an atomic per cent basis. The amount of solute which can be accommodated

in the solvent lattice before a new phase or a superlattice appears is an indication of the distortion being produced in the solvent. The greater the amount of solute which can be accommodated, the less is the distortion produced and the less will be the hardening effect. The chief difficulty in the application of this method of analysis is that it is dependent on the accuracy of the phase diagrams. Parts of many of the iron binary phase diagrams are not too well known. Using the phase diagrams in the ASM Handbook, the solubility has been listed in column four of Table III. Cobalt and chromium are reversed, but their solubilities are both very high, and other factors might be expected to be more important. Titanium is out of order with respect to molybdenum and tungsten, but the solubilities of these three elements are very similar. Silicon is the only element which is badly out of place. Jette and Greiner (11) showed a discontinuity in the lattice constant versus concentration curve at 9 atomic per cent silicon. If 9 atomic per cent is taken as the solubility instead of 26, the agreement is better.

## Yield Strength

The yield strengths vary almost directly with the tensile strength. The yield strength-atomic per cent plot (Fig. 4) is similar to the tensile strength plot except that cobalt and vanadium change places at the lower percentage and that the upper elements, silicon, titanium and tungsten, are grouped more closely together.

It is to be noted that the yield strength values are much lower than are usually expected for iron. This is no doubt the result of the hydrogen treatment. A larger grain size will lower the yield strength as Edwards and Pfeil (7) have shown, but the grain size of the chromium alloys (ASTM No. 3 - 4) is smaller than that at which Edwards and Pfeil obtained the maximum yield point; hence, grain size cannot be producing the low yield values in these alloys.

## Elongation and Reduction of Area

No attempt was made to correlate the elongation and reduction of area because they were so large that the accuracy of measurement, especially for reduction of area, was very poor. Also, it was observed that the extent of deoxidation materially

affected the ductility values. Those elements having little deoxidation power were less ductile than the others.

However, a few generalizations might be made. Most of the ductility values fall within a narrow range. The elongation values lie between 50 and 60 per cent, while a 90 to 95 per cent

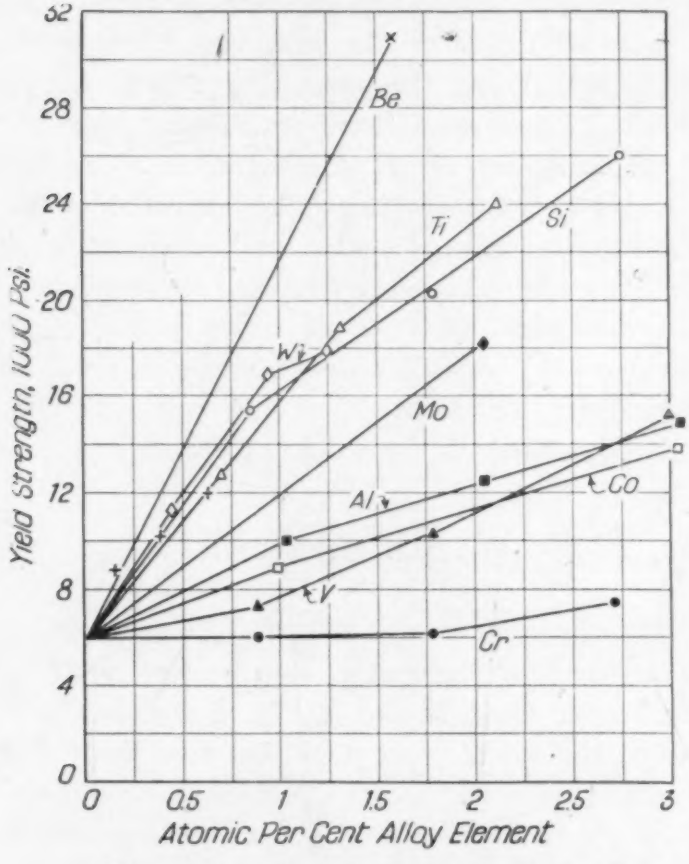


**Fig. 4—Yield Strength Versus Atomic Per Cent of Alloying Element.**

range includes most of the reduction of area values. Within any one alloy system the elongation and reduction of area values decrease with increase in alloy content as is to be expected from the increase in tensile strength produced.

## Slope - Intercept

The increase of the intercept of the true stress-strain curve is plotted against atomic per cent of alloying element in Fig. 5, and the slope of the straight line portion of the true stress-strain curve is plotted against the intercept of the curve at zero strain

in Fig. 6. There is apparently a direct relation between the slope and intercept. The greater the slope, the greater will be the intercept. With the exception of beryllium, the points for the alloys appear to lie along a straight line from the origin and with a slope of about 0.95. The rate of strain hardening is then equal to the unstrained strength divided by 0.95. The intercept at zero strain, which may be used as an index for the unstrained strength

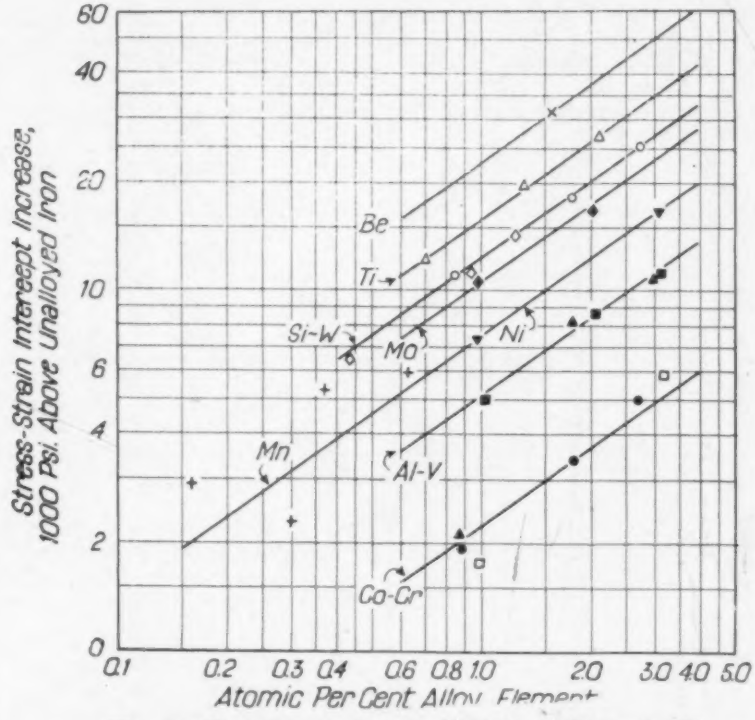


**Fig. 5—The Increase in the Unstrained Strength (Intercept of the Extrapolated Straight Part of the True Stress-Strain Curve at Zero Strain) Versus Atomic Per Cent of Alloying Element, Plotted Logarithmically. The n Value is Now 0.71. n Would Have the Same Value for Such a Plot for the Stress at Any Common Value of Strain.**

of an alloy, varies with concentration in exactly the same way as the tensile strength, discussed previously, except that the "n" value (slope of the log - log plot) seems to be a trifle less, namely about 0.71. This is not surprising, for the tensile strength is represented on the stress-strain curve by a point that shifts from a higher strain value to a lower strain value as the alloy is strengthened, and so is not a measure of strength at constant strain. Since the tensile strength and intercept are closely related, this also shows that the slope increases with an increase in tensile strength, hence the alloys with the greater tensile strength show the greater rate of strain hardening.

The nature of this relationship requires that the slope per unit of stress be a constant at any particular strain. In Tables I and II, the slope per unit stress at two values of strain are tabulated for all the alloys. These values were obtained by dividing the slope by the stress given by the extended straight line portion of the true stress-strain curve at the particular strain under consideration. The data indicate that with the exception of the beryllium and

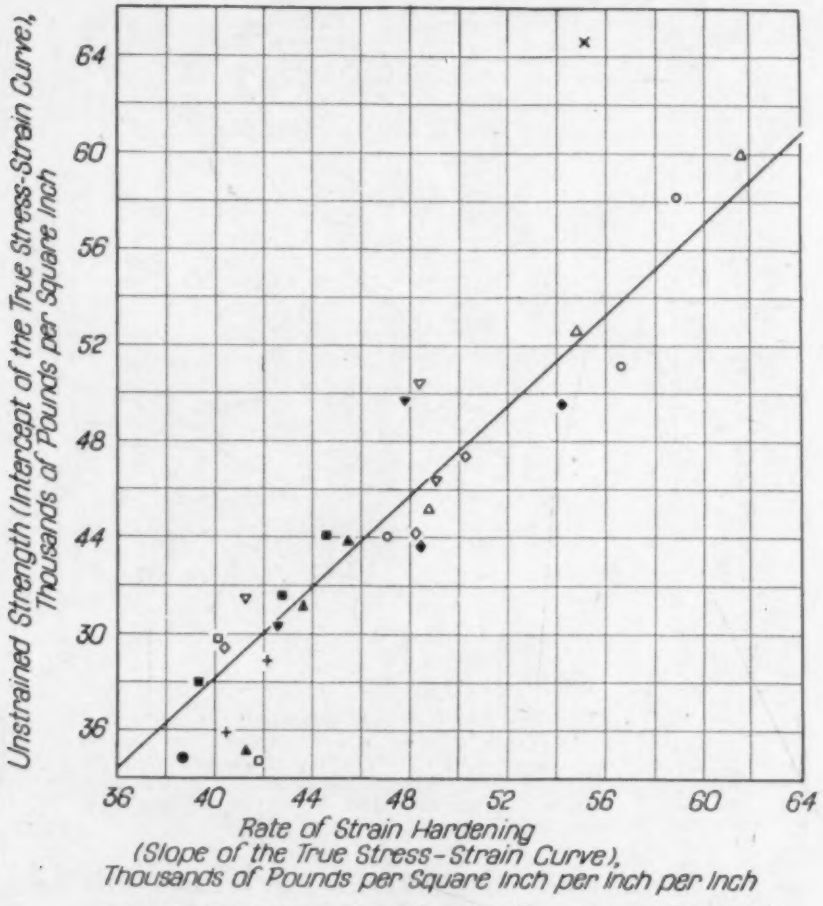


**Fig. 6—Unstrained Strength (the Zero Strain Intercept) Versus the Minimum Rate of Strain Hardening (the Slope of the Straight Part of the True Stress-Strain Curve). The Slope of the Line, Which Extends to the Origin, is 0.95.**

cobalt alloys, the slope per unit stress values fall within a narrow range for a given strain. For zero strain the range from 0.96 to 1.12 includes most of the data, while a 0.6 to 0.7 range includes most of the data at 0.6 strain; the scatter is almost within the limits of experimental accuracy. This constancy indicates that although the rate of work hardening increases with the addition of an alloying element, the rate of work hardening per unit of

hardness is approximately a constant for a given amount of deformation.

These regularities may perhaps be better described by referring to the schematic curves of Fig. 7. These curves all extrapolate to a common origin, and are so drawn that the slope of the straight part is 1.05 times the intercept at zero strain. Except for the curved parts, which are different for different alloying elements, and which are also sensitive to small amounts of carbon, nitrogen and probably oxygen, they could serve for an alloy of a particular

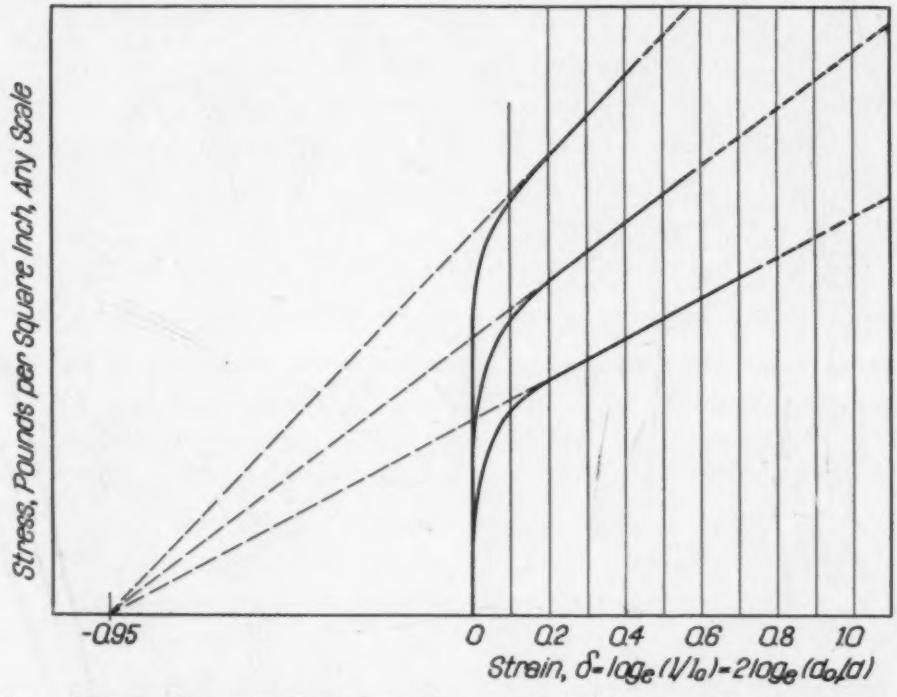


Fig. 7—Schematic True Stress-Strain Curves for any Alloying Element in the Appropriate Concentration. The Amount of Alloying Element Required is to be Obtained from Fig. 5, or Calculated by the Formula $(S - 35000) = kx^{.71}$ where k is the Intercept at One Atomic Per Cent in Fig. 5 and is Listed in Table IV.

composition, whatever alloying element might be used. It makes no difference whether a curve is obtained by using x per cent of element A or y per cent of element B; if the correct amount of alloying element is used the flow curves will coincide. From this it may be deduced that it is not to be expected that alloying elements will differ much in their effects on iron with respect to the amount of deformation thay may be obtained in tension before necking-down sets in; it does not seem that it would be profitable to investigate the deep-drawing characteristics of alloyed ferrite sheets.

**Table IV**
**Strengthening Coefficients for True Stress Intercept**

| | | |
|---|---|---|
| Beryllium | 23000 | |
| Titanium | 16000 | |
| Tungsten | 12000 | |
| Silicon | 12000 | |
| Molybdenum | 10000 | |
| Manganese | 7500 | (?) |
| Nickel | 7500 | |
| Aluminum | 5000 | |
| Vanadium | 5000 | |
| Cobalt | 2200 | |
| Chromium | 2200 | |

## Ternary and Quaternary Alloys

Nine ternary alloys and two quaternary alloys were prepared to determine what the combined effects of two elements might be. The data for these alloys (Table II) are in general agreement with those for the binary alloys in connection with the slope-intercept and the slope per unit stress values.

The tensile strengths were found to be approximately additive;

**Table V**
**Calculating Tensile Strengths by Simple Additivity, Taking Values from Tensile Strength vs. Atomic Per Cent Plot**

| Alloy | Measured T.S. | Calculated Value |
|---|---|---|
| 0.97 Ni-0.97 Si | 48550 | 48850 |
| 0.99 Ni-0.99 Cr | 39450 | 39000 |
| 1.01 Si-0.99 Cr | 43200 | 43000 |
| 1.04 Cr-1.04 Co | 34400 | 34800 |
| 1.03 V-1.03 Ni | 39450 | 41000 |
| 1.04 V-2.06 Ni | 45250 | 44800 |
| 1.02 V-3.00 Ni | 48150 | 48000 |
| 1.03 Mo-0.92 Cr | 42400 | 42700 |
| 0.07 Mn-0.97 Si | 43550 | 43900 |
| 1.02 Si-0.66 Al-1.07 V | 44400 | 47000 |
| 1.03 Ni-1.01 Cr-1.01 Si | 48600 | 49300 |

that is, the increase in tensile strength in a ternary alloy above that of the unalloyed iron is the sum of the increases produced by the particular amounts of the two added elements in their respective binary alloys.

Table V gives a comparison of the tensile strengths calculated in this manner with the measured values. The agreement is close in all cases with the exception of the quaternary silicon-aluminum-vanadium alloy. Data for the calculations were taken directly from Fig. 2 considering the strength of the iron base to be the 33,900 pounds per square inch value measured. In calculating the tensile strength of the 1 per cent vanadium - 3 per cent nickel alloy, the difference in tensile strength between a 3 per cent nickel alloy and

unalloyed iron and the difference between a 1 per cent vanadium alloy and unalloyed iron were obtained from the graph. These two differences were then added to the tensile strength of pure iron to give the calculated tensile strength of the ternary alloy.

The multiplying factor method of analysis was tried, but gave results which did not check the measured values nearly as well as the additivity method.

## Aging Effects

Two alloys, the three atomic per cent chromium alloy and the two atomic per cent molybdenum alloy, were heat treated to determine their aging characteristics. Samples which had been given a 50-hour wet hydrogen treatment similar to that given to the tensile specimens were heated in a lead bath for twenty minutes at 675 degrees Cent. (1250 degrees Fahr.) and quenched into water. The molybdenum alloy had a Vickers hardness of 110 as compared with a value of 105 in the annealed condition, while the chromium alloy had a hardness of 73, as compared with a value of 66 in the annealed condition.

Although the hydrogen treatment has not eliminated the aging characteristics entirely, it has produced a similar effect in both alloys. Austin (1) obtained widely different effects for these two alloys. It is probable that the hydrogen treatment has partially eliminated the materials producing the aging effect. Low and Gensamer (2) have shown that the yield point and aging in unalloyed iron can be completely eliminated by wet hydrogen treatment and have concluded that carbon and nitrogen are responsible for the effect. Since it has been shown that aging is caused by minor constituents in unalloyed iron, it is doubtful if the alloying elements have any direct effect on aging particularly if they do not have a limited solid solubility range. Consequently the effect of the alloying elements on aging would appear only indirectly through their effect on the presence of the minor constituent which causes aging.

## Conclusions

1. Resistance to deformation (stress at a certain strain, or tensile strength) is a power function of the concentration of alloying element in ferrite.

2. The strengthening curves for all the alloys studied are

parabolas of the same degree (having the same index, namely 0.71) so that $S - So = kX^{.71}$ where S is the strength of the alloy as stress at some particular strain. So is the strength of the unalloyed ferrite, X is the concentration, and k the strengthening coefficient. If tensile strength is used for S, the index becomes .75.

3. The strengthening coefficient increases as the limit of solubility for the alloying element in ferrite decreases. Silicon and cobalt are out of order by this criterion.

4. The fundamental flow curves (true stress-strain curves) for all the alloys are almost exactly similar, so that the rate of strain hardening is proportional to the strength. The slope of the straight part of the true stress-strain curves is numerically equal to 1.05 times the intercept of the curves at zero strain.

5. In ternary alloys, and probably in quaternary alloys, the strengthening effect is simply the ordinary sum of the strengthening effects of each of the alloying elements taken singly.

## Acknowledgments

The experimental work was done by Mr. Lacy while the holder of the International Nickel Company Graduate Fellowship in Metallurgical Engineering at Carnegie Institute of Technology. The International Nickel Company supplied many of the alloying elements and made the chemical analyses. Mr. N. B. Pilling, director of research for that company, made these arrangements and gave helpful advice. The low metalloid iron base was given by the Carnegie-Illinois Steel Corporation. The help of these organizations and of the staff of the Metals Research Laboratory is gratefully acknowledged.

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## DISCUSSION

**Written Discussion:** By George F. Comstock, metallurgist, The Titanium Alloy Manufacturing Co., Niagara Falls, N. Y.

In attempting to apply the strengthening curves given in this paper to some practically carbon-free alloys of iron, manganese and titanium that we have made and tested recently, considerable difficulty was encountered in following the directions given at the bottom of page 102 and top of page 103. It seems that in determining the calculated values for tensile strength given in Table V, the authors did not follow the procedure described in the text for the 1.00 per cent vanadium-3.00 per cent nickel alloy, but for that alloy a special curve was drawn, the results being lower than the additive values which would be obtained by the described procedure. Furthermore, the tabulated values for all the complex alloys seem to have been obtained, not directly from Fig. 2 as stated, but from another imaginary figure with the origin of all the curves at 33,900 pounds per square inch instead of about 32,200.

Using the authors' Fig. 1 in this way, with the assumption that all the curves started from 33,900 pounds per square inch at zero alloy per cent, and extrapolating the manganese curve to 1.5 per cent, some rough calculations were made on our alloys and compared with the actual test results. The alloys were made with pure electrolytic iron and manganese, but with a titanium alloy containing about ⅕ as much aluminum as titanium. All but two were found by analysis to contain not over 0.007 per cent carbon. The aluminum contents have not been determined. Each alloy was made in a 17-pound induction furnace and poured in a single ingot. The ingots were homogenized 4 hours at 2200 to 2250 degrees Fahr. (1205 to 1230 degrees Cent.), and forged into ⅞-inch round bars. Specimens from these bars were normalized 2 hours at 1750 degrees Fahr. (955 degrees Cent.), annealed 6 hours at 1200 degrees Fahr. (650 degrees Cent.), and furnace-cooled. The test results are compared with the calculated tensile strength in the Table A.

The actual tensile strengths are seen to be higher than the calculated in every instance except Nos. 5 and 6, but considering the roughness of the calculations and the difficulty of reading definite values from Fig. 1 of this paper, the agreement is reasonably good in all cases except the low titanium alloys 1, 4, and 7. These three alloys seem to be too hard and strong, or to indicate that titanium increasing from about 0.07 to 0.14 per cent softens and weakens the alloys. Probably this is due to nitrogen absorbed from the air in melting, which hardened the ferrite in Nos. 1, 4, and 7, but occurred in the form of an ineffective titanium compound when the titanium content was higher.

**Table A**

| Kind of Alloy | Low Mn. | | | Medium Mn. | | | Higher Mn. | | |
|---|---|---|---|---|---|---|---|---|---|
| Heat No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| Manganese content, per cent | 0.44 | 0.37a | 0.45 | 0.81 | 0.95 | 0.79 | 1.30 | 1.42b | 1.49 |
| Titanium content, per cent | 0.015 | 0.203 | 0.358 | 0.064 | 0.147 | 0.336 | 0.027 | 0.147 | 0.461 |
| Calculated tensile strength, pounds per square inch | 36900 | 37400 | 41900 | 39400 | 42400 | 43900 | 42900 | 45400 | 50400 |
| Actual tensile strength, pounds per square inch | 40600 | 38800 | 43100 | 42000 | 40000 | 43300 | 50700 | 48100 | 52400 |
| Yield strength, pounds per square inch | 19600 | 15600 | 18100 | 22000 | 16800 | 19100 | 34200 | 28500 | 32900 |
| Elongation in 2 inches, per cent | 51.0 | 56.5 | 52.5 | 55.0 | 56.5 | 51.0 | 48.5 | 46.0 | 46.5 |
| Reduction of area, per cent | 84.0 | 91.0 | 89.8 | 88.0 | 90.5 | 89.9 | 85.8 | 88.1 | 88.2 |
| Rockwell B hardness | 30. | 29. | 37. | 39. | 38. | 46. | 58. | 56. | 60. |
| Izod Impact Value (av. of 3) | 116. | 118.c | 127. | 98. | 113. | 124. | 138. | 122. | 146. |
| Grain size (1700 degrees Fahr. normalize) | 5. | 6. | 7. | 5—6 | 6—7 | 7. | 8. | 8. | 7. |

Notes:—(a) The carbon content of heat 2 was reported as 0.022 per cent. (b) That of heat 8 was reported as 0.015 per cent. (c) This is average of 2 tests; the third result was 55.

No direct comparison can be made between our yield strength values and those of the authors because they report no curve for manganese in Fig. 4. Our results check their work on titanium, however, in indicating that titanium increasing from about 0.2 to about 0.5 per cent (with no carbon of course) raises the yield strength about 3000 pounds per square inch. Our yield strengths on these samples were determined as the stress producing an elongation of 0.5 per cent under load. The effect of titanium above about 0.1 per cent in reducing the yield strength is strongly marked in Samples 2, 5 and 8 as compared respectively with 1, 4, and 7, presumably because of its transforming the nitrogen from solution in the ferrite to an ineffective titanium compound.

It is hoped that these results may be of interest in connection with the authors' paper, as showing how the principles they have developed may be applied to alloys prepared under somewhat more ordinary conditions, without the hydrogen treatment.

## Oral Discussion

R. P. VAN ZANDT:[1] What condition were these samples in regarding heat treatment at the time you made the tests? Were they melted down and were they cast bars?

DR. GENSAMER: They were melted in an induction furnace. We used an interesting trick in making the alloys. After they were melted the induction furnace coil was slowly raised so as to freeze the ingot from the bottom up. We did not want to make large heats in order to get sound specimens for tensile testing. This technique was successful in giving us ingots free from internal pipe. In the case of the alloying elements that were not good deoxidizers we added a little bit of carbon so we would get the reaction between iron oxide and carbon. The alloys were cooled in the crucible and then given an homogenization annealing, and then forged. After forging they were again annealed. Then they were cold-worked (cold-forged and cold-rolled a considerable amount) and again annealed to recrystallize them so that the grain size was substantially constant in all of the alloys. We wanted to have a series in which the grain sizes were as nearly the same as we could have them. The final

[1]Staff engineer, Caterpillar Tractor Company, Peoria, Ill.

treatment was annealing below the critical in wet hydrogen to get the carbon as low as possible without excessive grain coarsening.

SAMUEL EPSTEIN:[2] Your results on the strengthening effect of the elements on ferrite appear to have checked those of Professor Austin at Pennsylvania State College fairly closely. Were there any discrepancies? Chromium has a very mild strengthening effect whereas titanium has a very strong effect. I recall Professor Austin tried to theorize as to why the different elements had these different effects. Have you tried to do the same thing?

DR. GENSAMER: The same kind of speculations or correlations could be made. We found the best correlation was with the limit of solid solubility. I think in general we checked Professor Austin's results on hardness. You have a hard time making hardness correlate very well. Indentation hardness is affected by the whole shape of the stress-strain curve, and especially by the yield strength, which is affected more by little differences in composition, structure and treatment than the properties on which we have concentrated our attention (tensile strength, and slope and intercept of the true stress-strain curve).

Professor Austin discussed the aging of his alloys. Ours aged too, although probably somewhat less. Aging is going to affect hardness, more so than stress-strain curves.

DANIEL C. DRUCKER:[3] Dr. Gensamer has shown that curves for the rise in tensile strength against alloy percentages are parabolic with decreasing slope as the amount of alloy is increased. If we consider such curves for two alloys, say A and B, Dr. Gensamer has further indicated that the increase in strength due to n per cent of A and N per cent of B is equal to the sum of the increase due to A by itself and B by itself, i. e., $\Delta S = k_A n^m + k_B N^m$.

The point that troubles me is that if one adds n per cent of A and then forgets and adds N per cent more of A, the resulting increase in strength $\Delta S = k_A (n + N)^m$ will not check with $\Delta S = k_A n^m + k_A N^m = k_A (n^m + N^m)$.

DR. GENSAMER: In the range of concentrations considered here you get approximately the same result. If the plots of properties against concentration were straight lines, 1 per cent added to 2 per cent would make 3 per cent. As a first approximation they are straight enough so that you can just add them up and come out with a figure which is near enough to account for the tensile strength, considering deoxidation practice and so on. I do not think a more exact calculation would be worth while. The simple method given in the paper should agree with a more exact calculation to within one or two thousand pounds per square inch.

J. J. KANTER:[4] This is a discussion on elevated temperature testing technique which is apart from the discussion right now. Fig. 7 raises some interesting speculation on the significance of the extrapolation to negative true strain. In casting about for a meaning to ascribe the extrapolation, it might be imagined to imply a relationship between stress and strain under a reversal of the process of work hardening. The limit of the extrapolation at zero true-stress might be considered the idealization of the reversal situation, where the specimen had

[2]Engineer, Development and Research Dept., Bethlehem Steel Co., Bethlehem, Pa.

[3]Research engineer, Armour Research Foundation, Chicago.

[4]Materials research engineer, Research and Development Laboratories, Crane Co., Chicago.

been a large single grain, properly oriented for slip along the planes of maximum shear. The intercept true-stress, by this picture, would then represent the measure of hardening which our testing machine happens to pick up at the stage of reduction of the original uni-grained material represented by the original diameter of the test bar.

If such a conception of the extrapolation can be admitted, then one is immediately confronted with the possibility that the diameter of the test bar may have something to do with fixing the values found on a true stress-strain diagram. It would be of interest to know to what extent such a consideration has been explored.

DR. GENSAMER: I would be surprised if, in the range of specimen sizes we ordinarily work with, the diameter of the specimen should affect the results. We have had a good bit of experience with stress-strain curves with different sized specimens. We are pretty well convinced that you can change the size of the specimen without changing the stress-strain curve. Certainly you can use quarter-inch instead of 0.505-inch bars. Whether it will work over a wider range than that I do not know.

MR. KANTER: I wonder if that spread in diameter would be great enough to be sensitive to the sort of effect that might exist?

DR. GENSAMER: I am afraid I do not understand how such an interpretation of the significance of the negative strain at zero stress intercept would require that the size of the specimen should affect the results, starting with an annealed bar.

### Authors' Reply

We think it advisable, in view of the oral discussion by Dr. Drucker and the written discussion by Mr. Comstock, to go a little more into detail concerning the calculation of the tensile strength to be expected for ternary and quaternary alloys. We shall describe a method capable of yielding more exact results than the simplified method used in calculating the values in Table V of the paper. It was our opinion that the accuracy of the results did not justify taking the space necessary to describe this method, but the discussion has changed my opinion. By this method the calculated tensile strengths are in better agreement with the measured tensile strengths than by the method given in the paper.

It will be observed, in Fig. 3 (in which the logarithm of the increase in tensile strength is plotted against the logarithm of the concentration), that at any given value for the increase in tensile strength, the ratio of the concentration of any two elements producing this increase is the same; that is, it is unaffected by the choice of the value for the increase in tensile strength. This is a consequence of the parallelism of the lines in the log-log plot. For instance, 10,000 pounds per square inch increase is caused by 0.64 per cent titanium and by 1.92 per cent nickel, while 20,000 pounds per square inch increase is caused by 1.60 per cent titanium and by 4.80 per cent nickel. In both instances the ratio of the nickel to the titanium concentration is 3.0. So the titanium concentration can always be expressed as an equivalent nickel concentration by multiplying it by 3.0; that is, 1.0 per cent of titanium is equivalent to

3.0 per cent of nickel. The same holds true for any other group of elements.

The equivalent nickel concentrations of all the elements studied are listed herewith in Table B. Any other element, or a hypothetical element, would do as well as nickel for the reference element.

**Table B**
**Equivalent Nickel Concentrations (Atomic Per Cent)**

| | | | |
|---|---|---|---|
| Titanium | 2.97 | Nickel | 1.00 |
| Silicon | 2.15 | Aluminum | 0.56 |
| Tungsten | 2.15 | Vanadium | 0.56 |
| Molybdenum | 1.82 | Cobalt | 0.20 |
| Manganese | 1.33 | Chromium | 0.13 |

To calculate the tensile strength, it is simply necessary to convert the concentration of each element to the equivalent nickel concentration, add the equivalent nickel concentrations to get the total equivalent nickel concentration, look up the increase in tensile strength for this nickel content in Fig. 3, and finally add this figure to 32,300 pounds per square inch (the extrapolated value for unalloyed iron). This procedure has been followed in preparing Table C.

**Table C**
**Comparison of Tensile Strengths Calculated by the Use of Fig. 3 with Measured Tensile Strengths**

| Concentration Atomic Per Cent | Equivalent Nickel Concentration Atomic Per Cent | Total Equivalent Nickel Concentration Atomic Per Cent | Tensile Strength Increase From Fig. 3 psi. | Calculated Tensile Strength psi. | Measured Tensile Strength psi. | Deviation psi. |
|---|---|---|---|---|---|---|
| 0.97Ni-0.97Si | 0.97-2.08 | 3.05 | 14,200 | 46,500 | 48,550 | —2,050 |
| 0.99Ni-0.99Cr | 0.99-0.13 | 1.12 | 6,650 | 38,950 | 39,700 | — 750 |
| 1.01Si-0.99Cr | 2.17-0.13 | 2.30 | 11,400 | 43,700 | 43,200 | + 500 |
| 1.03Ni-1.03V | 1.03-0.58 | 1.61 | 8,750 | 41,050 | 39,450 | +1,600 |
| 2.06Ni-1.04V | 2.06-0.58 | 2.64 | 12,700 | 45,000 | 45,250 | — 250 |
| 3.00Ni-1.02V | 3.00-0.57 | 3.57 | 15,900 | 48,200 | 48,150 | + 50 |
| 1.04Co-1.04Cr | 0.21-0.13 | 0.36 | 2,800 | 35,100 | 34,400 | + 700 |
| 1.03Mo-0.92Cr | 1.88-0.12 | 2.00 | 10,300 | 42,600 | 42,400 | + 200 |
| 0.97Si-0.07Mn | 2.08-0.09 | 2.17 | 11,000 | 43,300 | 43,550 | — 250 |
| 1.03Ni-1.01Cr-1.01Si | 1.03-0.13-2.18 | 3.34 | 15,200 | 47,500 | 48,600 | —1,100 |
| 1.02Si-0.66Al-1.07V | 2.19-0.37-0.60 | 3.16 | 14,500 | 46,800 | 44,400 | +2,400 |

For eleven alloys, the mean calculated tensile strength is 100 pounds per square inch greater than the mean measured tensile strength. The average deviation is 900 pounds per square inch, with extreme deviations of —2050 pounds per square inch and +2400 pounds per square inch. The former, —2050 pounds per square inch, is for an alloy containing only nickel and silicon; it is the only alloy containing neither chromium, vanadium or manganese; it may have a tensile strength higher than the calculated value because of inadequate deoxidation. The other, with a deviation of +2400 pounds per square inch, contains small amounts of aluminum and vanadium; in Fig. 3, the points for both the 0.875 per cent vanadium and 1.03 per cent aluminum alloys lie well below the line that was drawn to conform to the rest of the data. The aluminum

alloy was especially low, about 1800 pounds per square inch below the line. The same anomaly seems to have been observed in both the binary and the ternary alloys.

In the calculations collected in Table V in the paper, the average deviation is less, namely 680 pounds per square inch, but the mean calculated tensile strength is 450 pounds per square inch more than the mean measured tensile strength, compared to 100 pounds per square inch more by the method of equivalent nickel concentrations.

In specific reply to Mr. Comstock's written discussion, I have calculated the tensile strengths by the method of equivalent nickel concentrations, with the results summarized in Table D.

**Table D**

**Calculated and Measured Tensile Strengths of Mr. Comstock's Alloys**

| Heat No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| Calculated Tensile Strength, psi. | 36700 | 39300 | 41800 | 39750 | 41700 | 43400 | 42000 | 44100 | 48200 |
| Measured Tensile Strength, psi. | 40600 | 38800 | 43100 | 42000 | 40000 | 43300 | 50700 | 48100 | 52400 |
| Deviation, psi. | —3900 | +500 | —1300 | —2250 | +1700 | +100 | —8700 | —4000 | —4200 |

For the first six alloys (the low manganese alloys) the mean calculated tensile strength is 860 pounds per square inch too low, with an average deviation of 1600 pounds per square inch, and extreme deviations of —3900 pounds per square inch and +1700 pounds per square inch. Considering the differences in methods of preparation, and the neglect of aluminum in the analyses, this agreement is very gratifying, and I am very grateful to Mr. Comstock for submitting these data.

For the high manganese alloys it should be observed that the highest of the alloys prepared by Mr. Lacy contained only half the manganese of the lowest of these three alloys. Could it be that these alloys are not single phased?

# HIGH SPEED TESTING OF MILD STEEL

By J. H. Hollomon and C. Zener

*Abstract*

*Some of the difficulties encountered in high speed testing of materials are purely mechanical, and may, therefore, be overcome with proper diligence. One difficulty, however, is associated with the unavoidable inertia of the test material itself. The intrinsic limitation which this puts upon high speed testing is discussed.*

*The literature is rich in data regarding the variation of the tensile properties of mild steel with rate of deformation, in the range of strain rates available with the usual testing machines. This data is so correlated that a reasonable extrapolation to high strain rates may be made regarding the tensile properties. By such an extrapolation, it is predicted that in mild steel the yield strength becomes equal to the tensile strength in the range of strain rates between 1 and $10^4$ sec.$^{-1}$, depending upon grain size and carbon content. The dynamic implications of an equality of the yield and tensile strengths is pointed out.*

FERROUS material is subjected often in service to impulsive loads. In certain applications it is only necessary that the material have a sufficiently high yield strength. In other applications, where deformation is inevitable, the shape of the plastic portion of the stress-strain curve is of paramount importance. The shape of this curve determines the speed of propagation of plastic deformation, (1)* and therefore the extent of the permanent damage. It is therefore important to know how the stress-strain relation depends upon rate of deformation. The direct determination of this relation at high rates of strain has always been accompanied by experimental difficulties occasioned by vibrations. The first purpose of this paper is to demonstrate that no amount of ingenious experimentation would enable one to determine directly the stress-strain relation with a reasonable accuracy at rates of loading over 100 ft./sec. The second

*The figures appearing in parentheses pertain to the references appended to this paper.

The statements or opinions expressed in this article are to be considered those of the authors and do not necessarily express the views of the Ordnance Department.

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purpose of this paper is to find what facts may be surmised concerning the stress-strain relation at high rates of loading by the extrapolation of known information obtained at lower rates of loading.

## Intrinsic Limitation to High Speed Tests

In the quasi-static tension test, one measures the force applied to the specimen as a function of the elongation. This force divided by the original cross sectional area is called, incorrectly, "stress." In

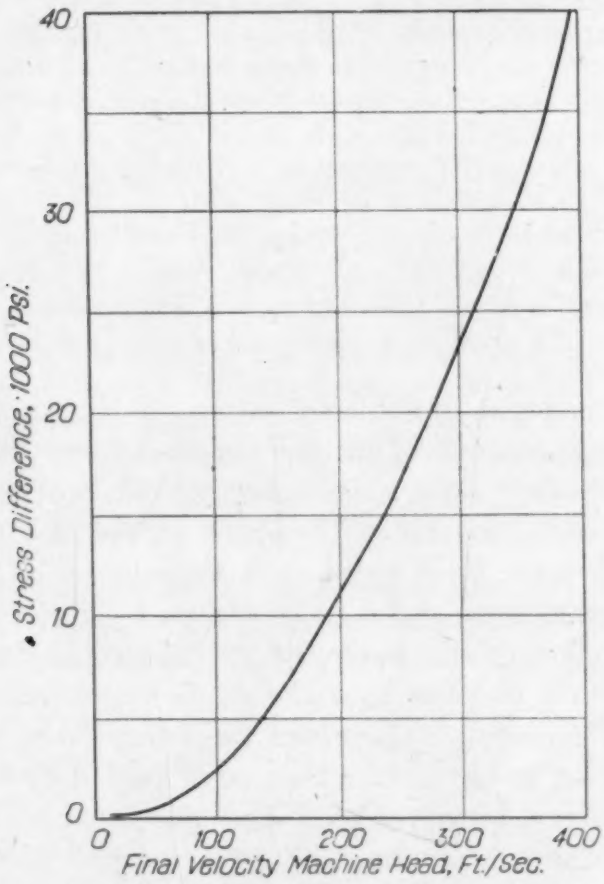


**Fig. 1—Stress Difference Between the Ends of a Test Specimen Uniformly Accelerated up to a Strain of 0.1.**

the dynamic tensile test one attempts to measure the same quantities. Often the vibrations of the apparatus and the specimen are of such magnitude that a precise determination of the force is not possible. The presence of this error is readily observable, however, for the vibrations are recorded by the stress-measuring device. There is another source of error, the presence of which is not obvious to

the experimenter. Two forces are actually applied to the specimen; one at the moving end and another at the stationary end. The difference in these forces is equal to the force necessary to accelerate the mass of the material between the two ends, and will be present as long as one end of the bar is accelerated. Since this difference in force exists, the "stress" is not uniform along the specimen. If this difference is of the same order of magnitude as the load applied, the lack of uniformity of the "stress" over the gage length is so great that the measurement of the stress at either end has little or no significance.

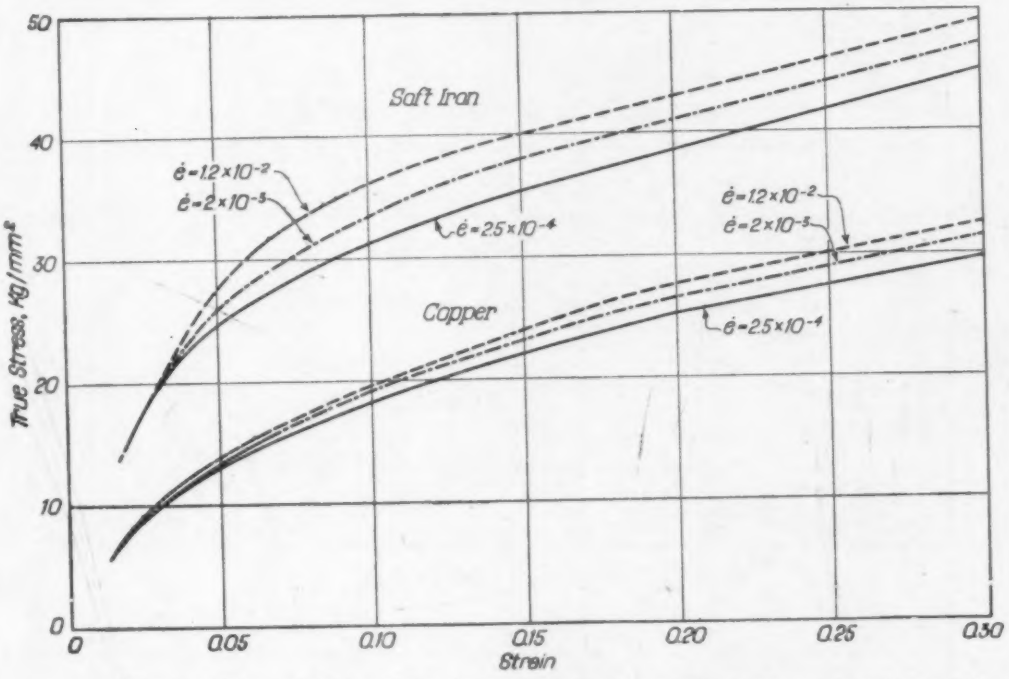


Fig. 2—Effect of Rate of Strain Upon True Stress-Strain Curve in Metals (8). (ė is the Strain Rate in Sec.$^{-1}$.)

The analysis of the stress difference at the two ends is given in Appendix A. Fig. 1 illustrates this stress difference in the particular case where the velocity of the head of the machine increases linearly with time, until a strain of 0.1 is reached. If the final velocity is reached at a smaller strain, the stress difference will of course be greater. The results indicate that in testing steels at velocities greater than 100 fps, the error introduced in this manner may be a large percentage of the measured "stress."

The rate of strain may be increased by decreasing the gage length as well as by increasing the speed of testing. Decreasing the gage length, however, increases the possibility of stress concentra-

tions, increases the uncertainty of the extrapolation to larger sizes, and increases the experimental difficulties. In order to obtain results applicable to material deformed at high speeds, it is advisable and perhaps necessary to extrapolate from lower strain rates.

## Interpretation of the Literature

In one respect all metals react similarly to an increase in testing speed; the stress-strain curve in the plastic region is raised as the speed is increased and the magnitude of the rise increases with in-

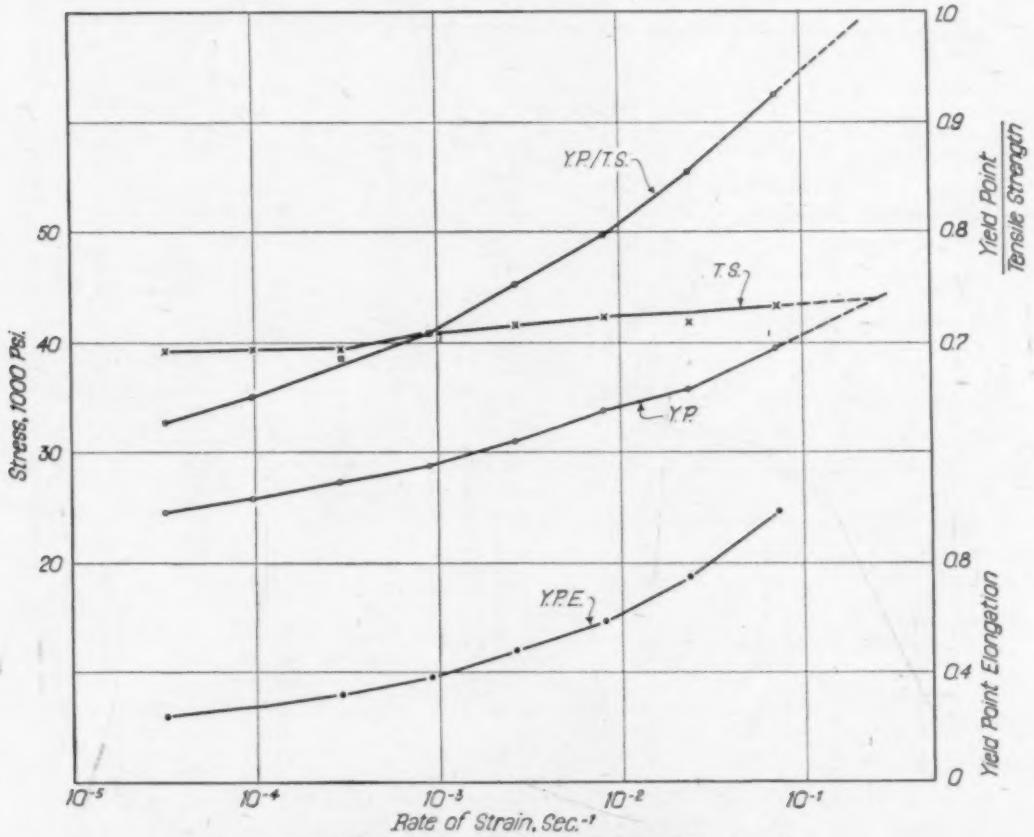


**Fig. 3—Effect of Speed on Tensile Properties (3).**

creasing stress (2) (Fig. 2). Iron and steels which exhibit a drop in load at the yield point behave in a characteristic manner. The yield point (lower) increases with increasing rate of strain faster than the tensile strength (3 to 11). This behavior is illustrated by data obtained by Winlock and Leiter (3) and presented in Fig. 3. The data presented in this figure were obtained from a steel containing 0.05 per cent carbon, annealed, and having a grain count of 90 per square inch at 100 magnification. (A. S. T. M. No. 7)

The lower yield point is used as the criterion for the beginning of plastic deformation, rather than the upper yield point, since the latter is dependent upon the surface condition, and shape of the specimen, and upon any slight eccentricity in loading. The lower yield point appears to be characteristic of the metal itself. Experiments have been performed in which the upper yield point was raised as high as, or higher than, the tensile strength, even in quasi-static tests. The effect of speed on materials with upper and lower yield is presented schematically in Fig. 4. The stress-strain relation for

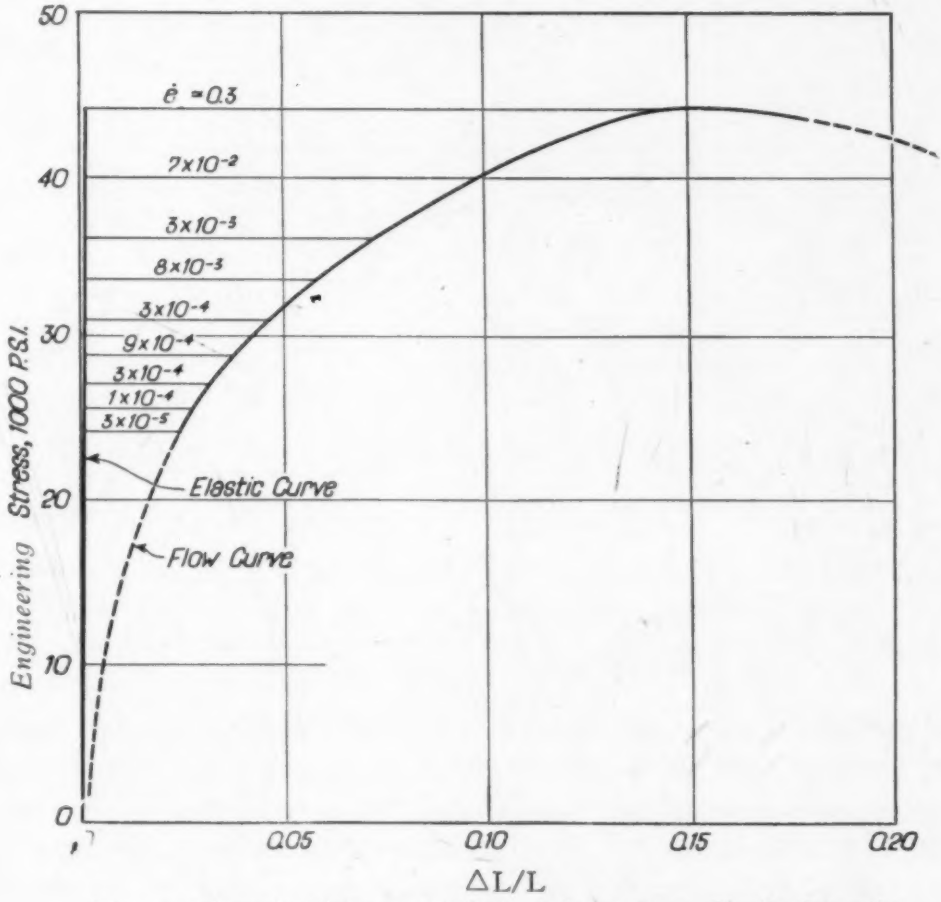


Fig. 4—Schematic Diagram of Effect of Speed Upon Tensile Properties (Data from Fig. 3). (ė Refers to the Strain Rate in Sec.$^{-1}$.)

such materials can be considered as made up to two curves essentially independent of rate of strain joined by horizontal lines. The first part of the total stress-strain curve is elastic; in the second part, inhomogeneous deformation occurs; and in the third part, the material undergoes homogeneous deformation accompanied by work hardening and sensible reduction of area. In this figure the slight effect of speed

beyond the lower yield point is neglected. As the speed is increased, the horizontal portion of the stress-strain curve rises, and the amount of strain at this lower yield point increases.

During the second part of the deformation, the strain occurs by the formation and spreading of Lüders' bands. In each Lüders' band the strain is equal to the yield point elongation. Only after all of the specimen has been traversed by Lüders' bands does it deform homogeneously. From Fig. 4 it appears that a critical strain rate exists, above which the specimen will fail by shear along the first and only

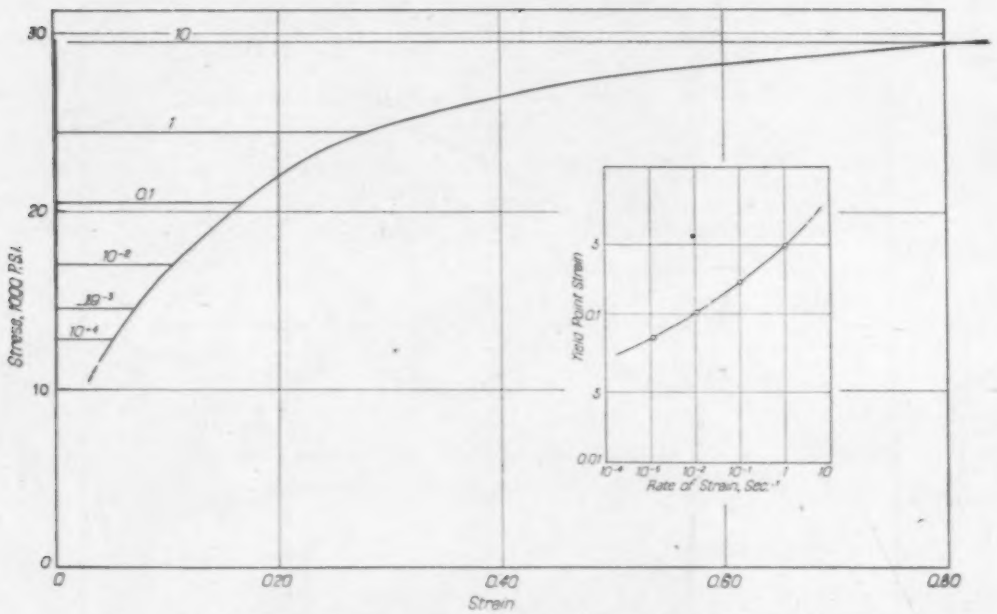


Fig. 5—Schematic Diagram of Effect of Speed Upon Shear Properties. [Horizontal Lines Refer to Different Strain Rates (Sec.$^{-1}$.)]

Lüders' band formed, and homogeneous deformation will not occur. The usefulness of the schematic diagram in Fig. 4 for tension suggests that a similar one be constructed for pure shear. Such a diagram is presented as Fig. 5. This diagram illustrates the approximate behavior in shear of the same steel to which Fig. 4 pertains. Since in pure shear, the static stress-strain curve does not pass through a maximum as does the force-elongation curve for tension, a critical rate of shear beyond which all deformation is confined to a single band does not necessarily exist. The yield point elongation, and hence the elongation associated with each Lüders' band, increase rapidly with increasing rate of strain. When, however, this yield point elongation is so large that the temperature rise of the material in the band is several hundred degrees centigrade, the "static" stress-

strain curve will be lowered. In this case the deformation to fracture may likewise be confined to a narrow band.

An indirect substantiation of this conclusion may be found in the work of Itihara (14). He found that by raising the rate of strain by a factor of 4 x $10^4$ over that in the quasi-static tests, the yield point was doubled, while the maximum stress remained essentially unchanged. The details of the stress-strain curve were obscured, however, by vibrations. The curves in Figs. 3, 4, and 5 refer specifically to a single type of steel tested by Winlock and Leiter (3). The

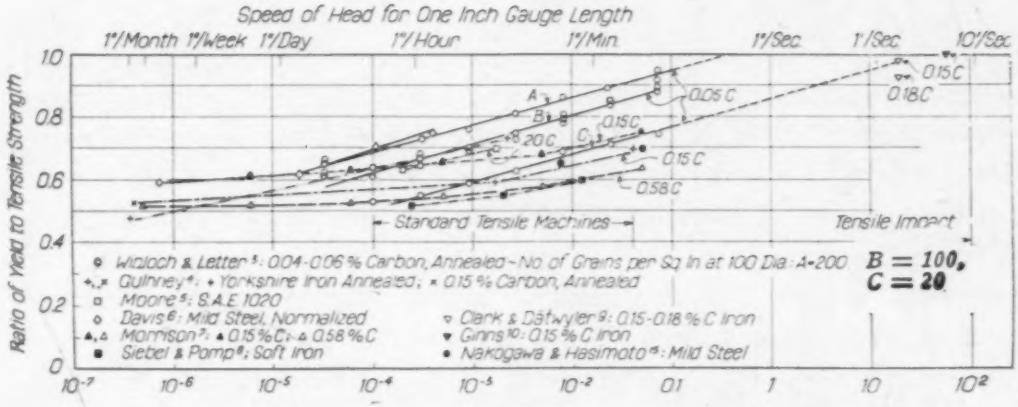
Speed of Head for One Inch Gauge Length
1"/Month 1"/Week 1"/Day 1"/Hour 1"/Min. 1"/Sec. 1'/Sec. 10'/Sec.
Ratio of Yield to Tensile Strength
0.05 C
0.15C
0.18C
0.20C
0.15 C
0.58C
Standard Tensile Machines
Tensile Impact
B = 100,
C = 20
Winlock & Letter[5]: 0.04-0.06 % Carbon, Annealed - No. of Grains per Sq. In. at 100 Dia.: A-200
Guilney[4]: + Yorkshire Iron Annealed; × 0.15 % Carbon, Annealed
Moore[5]: S.A.E. 1020
Davis[6]: Mild Steel, Normalized
Morrison[7]: ▲ 0.15 % C; △ 0.58 % C
Siebel & Pomp[8]: Soft Iron
Clark & Dätwyler[9]: 0.15-0.18 % C Iron
Ginns[10]: 0.15 % C Iron
Nakagawa & Hasimoto[15]: Mild Steel

**Fig. 6—Effect of Speed on Relation Between Yield Point and Tensile Strength.**

general features of these curves will apply to any steel with a lower yield point. In particular, the lower yield stress approaches the tensile strength at high rates of deformation. In an attempt to find those factors which influence the rise of the lower yield point with rate of strain an extensive search was made in the literature of the effect of speed on the tensile test. Most of the investigators recorded only the upper yield point. Fig. 6 shows all the data in which the lower yield strengths, as well as the tensile strengths, were reported as a function of the rate of strain.

In all cases the ratio (lower yield stress/tensile strength) approaches an asymptote at low rates of strain, and varies nearly logarithmically at higher rates of strain. The ratio is dependent upon the carbon content, decreasing as the carbon content increases. For a given carbon content the ratio is larger, the smaller the grain size. The absolute magnitude of the ratio as well as its dependence upon rate of strain should be dependent upon the microstructure, as well as upon carbon content, but a detailed study of the effect of these variables is lacking. The values of this ratio obtained from the ten-

sile impact machine are consistent with the extrapolation of the data obtained from the standard testing machines (9), (10).

Although the unit of rate of strain used in Fig. 6, namely $sec^{-1}$ is the most logical unit, it is one for which few have any physical grasp. In order to give the rates more concrete expression, an interpretation of these units is presented along the top margin in terms of the rate at which the head of a 1-inch gage length specimen must move to produce the appropriate rate of strain.

The strain rate at which the yield strength becomes equal to the tensile strength may be estimated by extrapolation of the observations in Fig. 6 to higher strain rates. For the steels represented in this diagram, the ratio between the yield and tensile strength becomes equal to unity at strain rates between 1 and $10^4$ $sec^{-1}$. This critical strain rate is higher, the higher the carbon content and the larger the grain size. At and beyond this critical strain rate, the load in the tensile test will not rise after yielding. All the uniform elongation will occur through the formation of Lüders' bands. If the geometry of the specimens is such that the Lüders' bands form only along a single parallel set of planes, then plastic deformation may be confined to a single such band, with a consequent drop in the energy for rupture. At such strain rates, the velocity of propagation for shear deformation vanishes.

## Appendix A

In this appendix the calculation is carried out for the difference in stress at the two ends of a tensile specimen during a high speed test.

The difference between the forces acting at the two ends is equal to the sum of the products of all the elements of mass in the gage length and their respective accelerations:

$$\Delta f = \Sigma \delta m_k a_k \qquad (1)$$

During the entire test the right member of Eq. (1) is given very nearly by the relation:

$$\Sigma \delta m_k a_k = \tfrac{1}{2} \rho A l a \qquad (2)$$

where $\rho$, A and l refer to the original density, cross-sectional area, and gage length, respectively, and where $a$ refers to the accelerations of the moving end. Thus, before necking, the acceleration

varies linearly along the specimen from 0 to a. Here the mean acceleration is ½a. After the onset of necking, half the specimen has practically no acceleration, the other half has nearly the acceleration *a*. Again the mean acceleration is given nearly by ½a.

After substituting Eq. (2) into Eq. (1), and dividing the resulting equation by A, one obtains for the stress difference:

$$\triangle S = \tfrac{1}{2}\rho la \qquad (3)$$

If it is assumed that the moving end of the specimen has acquired the velocity v by the time the specimen has elongated a distance $\triangle l$, then the maximum value of $\triangle S$ during this elongation will be a minimum if it is a constant. This constant is given in terms of v and by the equation:

$$a = v^2/2\triangle l \qquad (4)$$

The substitution of the relation into Eq. (3) gives the final equation:

$$\triangle S = \tfrac{1}{4}\,(l/\triangle l)\rho v^2 \qquad (5)$$

In the above equation, all quantities must, of course, be expressed in a consistent set of units. The corresponding equation for iron or steel in which S is expressed in units of psi, and v in units of ft/sec.:

$$\triangle S = 0.027\,(l/\triangle l)\,v^2 \text{ in psi.} \qquad (6)$$

This equation is plotted in Fig. 1 for the typical case of $\partial l = 0.1$.

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13. C. W. MacGregor, American Society of Mechanical Engineers, Vol. 53, A.P.M. 87, 1931.
14. M. Itihara, *Technology Reports,* Tohoku Imperial University, Vol. 11, 1933, p. 16, 512; Vol. 12, 1936, p. 63.
15. Nokahawa and Hasimoto, *Transactions,* Society of Mechanical Engineers, Japan, Vol. 5, 1939, p. 5.

## DISCUSSION

**Written Discussion:** By Ralph Leiter, metallurgist, and Joseph Winlock, chief metallurgist, Edward G. Budd Manufacturing Co., Philadelphia.

The analysis of the stress difference at ends of test pieces due to acceleration is very interesting and valuable. Fortunately the bulk of impact testing has been done at velocities under 20 feet per second where the acceleration effect is negligible.

We are in complete agreement with the authors on their interpretation of the behavior of annealed iron and mild steel. We predicted premature fractures in low carbon steel when the lower yield point exceeded the tensile strength, page 181 of author's reference 3 (A.S.M.). We subsequently tested all three steels at a speed of 40.5 inches per inch of gage length per minute or 0.67 inches per second and as predicted from Fig. 6, steel A fractured in the region of the first Lüders' band with no plastic deformation while steels B and C deformed in the regular manner. We have no facilities for testing at higher rates of deformation so we are unable to confirm the extrapolation of the curves for steels B and C.

### Oral Discussion

J. J. KANTER:[1] A great deal of experimentation on high speed testing has been done at Crane Research Laboratories by Mr. Watt Smith. This work has served to give us certain views on the subject apropo of the present paper.

One of the most significant things in this paper, as we see it, is the importance which Lt. Hollomon and Dr. Zener have attached to consideration of inertia of the actual test material. This is a factor in high velocity test which we have noted as being amazingly important. When tests are made at high striking velocities of 100 feet per second and higher, one begins to observe that the specimen of metal needs no support whatsoever to break itself. The sudden acceleration imparted to it, of itself, induces forces great enough to overcome the strength of the material, whether tension or transverse force is being applied to the material. The forces are so great that just the specimen suspended in air, upon being suddenly accelerated will become distorted or even break.

[1]Materials research engineer, Crane Co., Chicago.

Such phenomena are rather familiar to us if we think of them in homelier terms than test specimens of metal.

It seems, though, that most of the thinking which has been done along the lines of high speed testing has heretofore been too greatly influenced by the familiar static testing procedures, which when translated to high velocities just will not work. Thus, this paper by Lt. Hollomon and Dr. Zener is really the first one to recognize the influence of the internal inertia of the substance under test. Thus, now we are perhaps beginning to get somewhere on this subject of high velocity testing.

On the matter of the increase of yield point with increase of testing velocity, while in principle we would agree with the authors that the strength and yield merge with high testing velocity, perhaps the quantitative conclusions which are presented are open to some question. The authors base their yield curve upon the Winlock and Leiter data. There is some question as to just what the quantitative significance is of the yield points which Messrs. Winlock and Leiter measured, since such measurements are subject to all of the inertia effects of the testing machine itself.

It is not entirely clear to us just what physical significance there is in showing the incidence of yield point and tensile strength by extrapolation, anyway. That incidence presupposes a certain amount of strain associated with it. However, under high test velocities there might be an incidence of forces such as we do not observe in static testing unless a considerable amount of plastic strain is associated with it. It is the hope that the authors can clarify a little further the concept upon which they attach a significance to the extrapolation which has been made.

On the whole, we feel that the subject of high velocity testing has been presented from a somewhat fresh viewpoint and affords an approach to the subject not hampered by the limitations of static testing.

R. P. VAN ZANDT:[2] I wonder if the authors would show on the blackboard what the stress-strain curves would look like for different rates of loading. I have seen some stress-strain curves of bars broken in tension by the impact of a pendulum, and stresses measured by some sort of strain gage apparatus.

SAMUEL EPSTEIN:[3] I would like to ask whether within the rates of loading you used was there a tendency toward a more brittle type of fracture at the faster rates of loading. Was more or less energy absorbed at the higher rates? Were you able to apply rates of loading fast enough to give a brittle fracture in mild steel?

### Authors' Reply

We wish to thank Mr. Kanter for his kind remarks on the importance of pointing out the inertial effects. We do not believe that the inertial effects of Winlock and Leiter's machine altered significantly their observed yield strengths. Their highest speeds were actually comparatively low, corresponding to a strain rate less than 0.1 inch per second. As to the physical significance of the equality of the yield and tensile strength, I wish to refer to the

[2]Staff engineer, Caterpillar Tractor Co., Peoria, Ill.
[3]Engineer, Development and Research Department, Bethlehem Steel Co., Bethlehem, Pa.

work of O'Donnell, who pointed out that the rate of propagation of plastic waves is proportional to the slope of the elongation curve. From that work, it follows that if your curve is flat, that is, if it does not rise, the rate of propagation will be zero and so all deformation must pile up.

In response to Mr. Van Zandt, Fig. A is presented showing an actual example of the effect of strain rate upon a load-elongation curve.

In reply to Mr. Epstein, we wish to point out that none of the experiments discussed in this paper have been performed by ourselves. We are not aware

Fig. A—Examples of Effect of Speed (After Winlock and Leiter).

of any cases reported in the literature where one can pass from a ductile to a brittle type of fracture in the ordinary tensile test specimen merely by increasing the speed of test without also introducing a notch or lowering the temperature of the test.

We are happy to receive the discussion by Messrs. Leiter and Winlock, in which they confirm the prediction that failure of mild steel at speeds above which the lower yield strength is equal to the tensile strength, occurs in the region of the first and only Lüders' band formed.

# THE EFFECT OF HEAT TREATMENT AND CARBON CONTENT ON THE WORK HARDENING CHARACTERISTICS OF SEVERAL STEELS

By John H. Hollomon

*Abstract*

*The true stress-strain curves for several carbon steels were determined. Both carbon content and strength level serve to increase the rate of strain hardening for these steels, irrespective of their microstructure. The strength and rate of work hardening specify completely the tensile plastic properties of metals. The study of the effect of composition of steel on the plastic properties has been reduced to the study of the effect of alloying elements on these parameters.*

N any application of steel in structures which undergo plastic deformation the rate of strain hardening may be of more importance to the proper choice of the steel than the yield or tensile strengths. The effects of composition and heat treatment on the work hardening characteristics of steel have received little attention. The results of ordinary tensile tests are usually plotted in the form of load elongation curves, but such curves are of little aid in the study of the behavior of metals during plastic deformation.

Ludwig[1] suggested as early as 1909 that a more profitable method would be to plot the true stress as a function of the strain defined as;

$$q = \int_{Lo}^{L} \frac{dL}{L} = \ln \frac{L}{Lo} \qquad (1)$$

where q = natural or true-strain.
Lo = arbitrary gage length.
L = gage length after deformation.

[1] P. Ludwig, "Elemente der technologischen Mechanik," Berlin, 1909, Julius Springer.

The statements or opinions in this article are those of the author and do not necessarily express the views of the Ordnance Department.

A paper presented before the Twenty-fifth Annual Convention of the Society, held in Chicago, October 18 to 22, 1943. The author, Lt. J. H. Hollomon, is stationed at the Laboratory of Research and Development, Watertown Arsenal, Watertown, Mass. Manuscript received May 13, 1943.

MacGregor[2] pointed out that in this form Eq. (1) could not be used after necking of the bar begins for then the length in which the strain is occurring is indeterminant. Assuming, however, that the volume of a thin disc in the region undergoing deformation remains constant, we may write

$$A_oL_o = AL; \quad \text{or} \frac{Ao}{A} = \frac{L}{Lo} \qquad (2)$$

where $A_o$ and $L_o$ refer to the initial area and length of the disc respectively and A and L to the area and length after deformation. With the substitution of Eq. (2), (1) becomes

$$q = \ln \frac{Ao}{A} \qquad (3)$$

From the measurement of the diameter of the bar, and by substitution in Eq. (3) the average true-stress* may be plotted as a function of this natural or true-strain. MacGregor stated that for steels the relation between true-stress and true-strain is linear approximately after the tensile strength is reached, indicating that the rate of increase of strength with strain due to work hardening is constant from the beginning of necking.[2] MacGregor also recorded stress-strain curves in this form for various materials at room and elevated temperatures.[3] Gensamer and co-workers[4, 5] investigated in some detail the effect of transformation temperature on the slopes of the stress-strain curves for several steels. They reported that for 0.78 per cent carbon steel the rate of work hardening was independent of the austempering temperature. The variation in the stress-strain curves for steels quenched and tempered at various temperatures was not investigated. They reported that the rate of strain hardening was independent of the metallographic structures studied, however their data shows an increase in rate of work hardening as the strength increases due to lowering the austempering temperature. They did not investigate the effect of carbon content. From the limited data on two steels[5] it may be inferred that the effect of manganese is to raise the rate of increase of strength with strain due to work hardening.

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[2]C. W. MacGregor, *Transactions*, American Institute of Mining and Metallurgical Engineers, Vol. 124, 1937, p. 208.

*It is recognized, of course, that the linear part of the stress-strain curve represents only an average, since the stresses are not constant across a necked region.

[3]C. W. MacGregor and L. E. Welch, *Metals Technology*, September, 1942.

[4]M. Gensamer, E. B. Pearsall and G. V. Smith, TRANSACTIONS, American Society for Metals, Vol. 28, 1940, p. 380.

[5]M. Gensamer, et al.: TRANSACTIONS, American Society for Metals, Vol. 30, 1942.

## Test Procedure

The preliminary experiments were performed on specimens representative of two types of steels taken from ¼-inch plate of the following compositions:

| Steel No. | C | Mn | Si | S | P | Ni | Cr | Mo | Al |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.44 | 0.81 | 0.25 | 0.022 | 0.021 | Nil | 0.035 | Nil | 0.007 |
| 2 | 0.19 | 0.49 | 0.205 | 0.030 | 0.016 | 1.83 | 0.005 | 0.24 | 0.01 |

from ½-inch round bars of the following compositions:

| Steel No. | C | Mn | Si | S | P | Ni | Cr | Mo |
|---|---|---|---|---|---|---|---|---|
| 3 | 0.49 | 0.66 | 0.18 | 0.021 | 0.016 | Nil | Nil | Nil |
| 4 | 0.20 | 0.35 | 0.03 | 0.025 | 0.017 | Nil | Nil | Nil |

The specimens were rough-machined, heat treated as outlined in Table I, finished-machined as illustrated in Fig. 1, and pulled in a

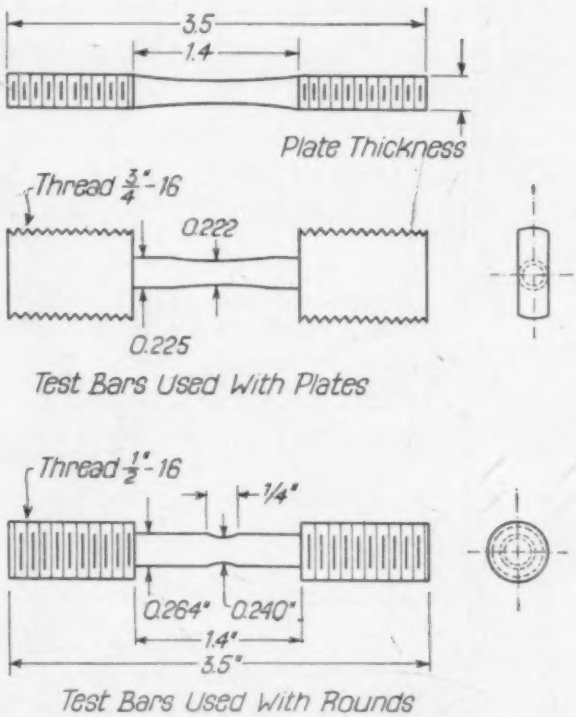


**Fig. 1—Sketches of Test Specimens.**

Riehle, beam-type, testing machine. A special clamp, with two dial gages, fitted between the shoulders of the specimens, was used to measure the elongation. After the yield point was reached the diameter of the specimen was measured by a knife edge micrometer.

**Table I**
**Heat Treatment of Metals**

| Spec. No. | Composition | Treatment | | | | | | | | Observed Microstructure |
|---|---|---|---|---|---|---|---|---|---|---|
| 1-1 | Steel 1 | 1525° F. | Quench | $H_2O$ | Draw | 800° F. | for | 1 | Hour | tempered martensite |
| 1-2 | Steel 1 | 1525° F. | Quench | $H_2O$ | Draw | 1000° F. | for | 1 | Hour | tempered martensite |
| 1-3 | Steel 1 | 1525° F. | Quench | $H_2O$ | Draw | 1100° F. | for | 1 | Hour | tempered martensite |
| 1-4 | Steel 1 | 1525° F. | Quench | $H_2O$ | Draw | 1275° F. | for | 1 | Hour | tempered martensite |
| 2-1 | Steel 2 | 1575° F. | Quench | $H_2O$ | Draw | 600° F. | for | 1 | Hour | tempered martensite |
| 2-2 | Steel 2 | 1575° F. | Quench | $H_2O$ | Draw | 800° F. | for | 1 | Hour | tempered martensite |
| 2-3 | Steel 2 | 1575° F. | Quench | $H_2O$ | Draw | 1100° F. | for | 1 | Hour | tempered martensite |
| 2-4 | Steel 2 | 1575° F. | Quench | $H_2O$ | Draw | 1275° F. | for | 1 | Hour | tempered martensite |
| 3-1 | Steel 3 | 1600° F. | Quench | $H_2O$ | Draw | 600° F. | for | 1 | Hour | tempered martensite |
| 3-2 | Steel 3 | 1600° F. | Quench | $H_2O$ | Draw | 800° F. | for | 1 | Hour | tempered martensite |
| 3-3 | Steel 3 | 1600° F. | Quench | $H_2O$ | Draw | 1000° F. | for | 1 | Hour | tempered martensite |
| 3-4 | Steel 3 | 1600° F. | Quench | Salt | to | 800° F.* | for | 2 | Hours | Bainite |
| 3-5 | Steel 3 | 1600° F. | Quench | Salt | to | 1000° F.* | for | 1 | Hour | Fine pearlite |
| 3-6 | Steel 3 | 1600° F. | Quench | Salt | to | 1200° F.* | for | 2 | Hours | Coarse pearlite |
| 3-7 | Steel 3 | 1600° F. | Quench | $H_2O$ | Draw | 1300° F. | for | 10 | Hours | Spheroidite |
| 4-1 | Steel 4 | 1600° F. | Quench | $H_2O$ | Draw | 200° F. | for | 1 | Hour | Fine pearlite |
| 4-2 | Steel 4 | 1600° F. | Quench | $H_2O$ | Draw | 400° F. | for | 1 | Hour | Fine pearlite |
| 4-3 | Steel 4 | 1600° F. | Quench | $H_2O$ | Draw | 800° F. | for | 1 | Hour | Fine pearlite |
| 4-4 | Steel 4 | 1600° F. | Quench | $H_2O$ | Draw | 1000° F. | for | 1 | Hour | Fine pearlite (slightly spheroidized) |
| 4-5 | Steel 4 | 1600° F. | Quench | Salt | to | 1200° F.* | for | 2 | Hours | Coarse pearlite |
| 4-6 | Steel 4 | 1600° F. | Quench | $H_2O$ | Draw | 1200° F. | for | 1 | Hour | Fine pearlite (slightly spheroidized |
| 4-7 | Steel 4 | 1600° F. | Quench | $H_2O$ | Draw | 1300° F. | for | 10 | Hours | Fine pearlite (spheroidized) |

*Temperature of salt bath.

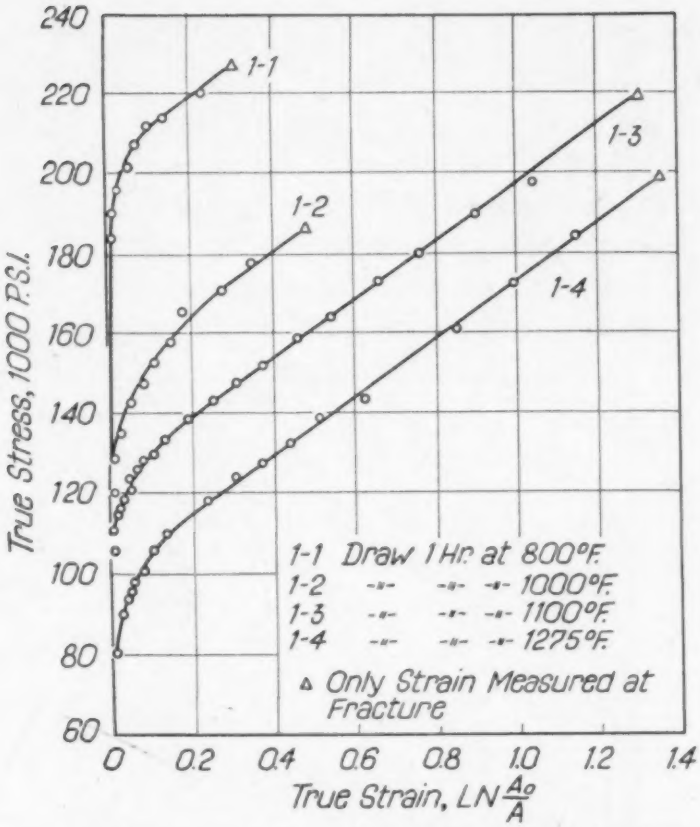


Fig. 2—True Stress Versus True Strain for Steel No. 1 (0.44 Per Cent Carbon). (For Different Tempering Temperature). Quenched (Water) 1525 Degrees Fahr.

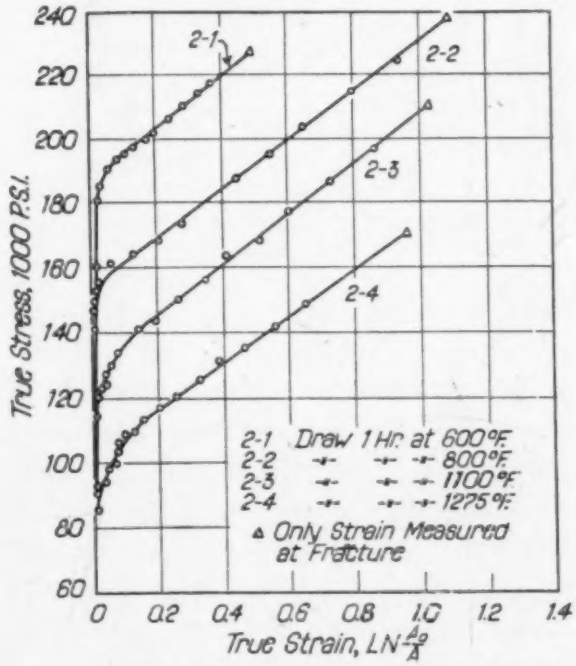


**Fig. 3—True Stress Versus True Strain for Steel No. 2 (0.19 Per Cent Carbon-1.8 Per Cent Nickel). (For Different Tempering Temperatures). Quenched (Water) 1575 Degrees Fahr.**

The load was held for several minutes before the micrometer was read and the time for each test averaged about 1 hour.

## Results and Discussion

In Figs. 2 and 3 are presented the data obtained for the specimens taken from the plates of composition 1 and 2. The specimens were quenched in water from 1575 degrees Fahr. (855 degrees Cent.) and drawn to the temperatures indicated on the graphs. The straight

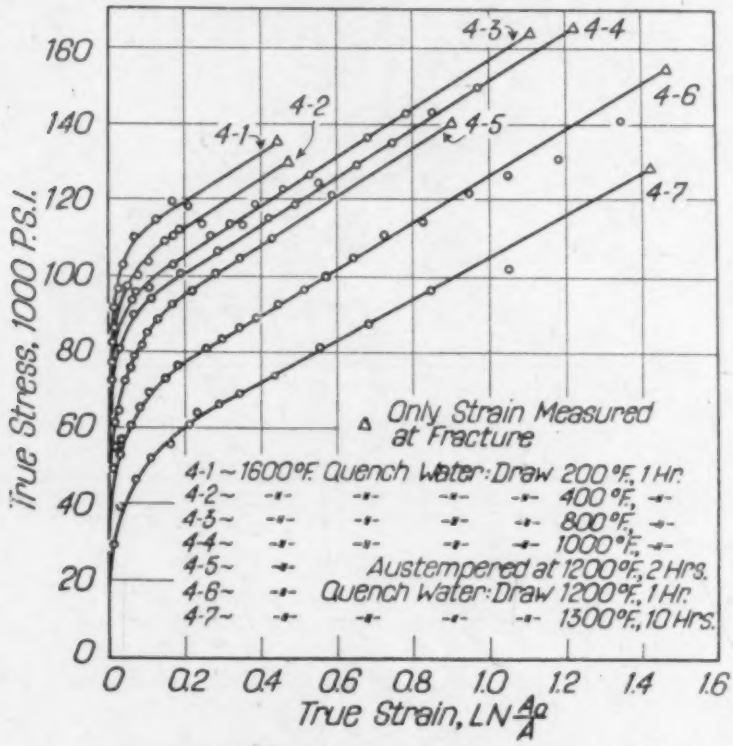


Fig. 4—True-Stress Versus True-Strain for Different Heat Treatments. Steel No. 4 (S.A.E. 1020).

lines which determine best the slopes after a strain of about 0.2, are drawn through the data. Since the load at fracture is difficult to measure, the approximate fracture stress was determined by continuing the straight line to the strain measured at fracture. Necking begins in the bar approximately at that strain after the yield stress in the true-stress true-strain curve, at which the curve becomes linear[2] (Figs. 2, 3, 4, 5). The slopes of the curves between tensile and fracture stress for both steels increase slightly with drawing temperature (Figs. 2 and 3). The 1.8 per cent nickel, a 0.20 per cent

[2]C. W. MacGregor, *Transactions*, American Institute of Mining and Metallurgical Engineers, Vol. 124, 1937, p. 208.

carbon alloy exhibits about the same rate of increase of strength with strain as the 0.45 per cent carbon alloy (Figs. 2 and 3).

Samples taken from the 0.20 per cent carbon (steel No. 4) round bars were heat treated to produce pearlite of different lamellar spacings and spheroidized cementite. The true-stress true-strain curves for these samples are presented as Fig. 4. The specimens of composition No. 3 were heat treated as indicated in Table I and the

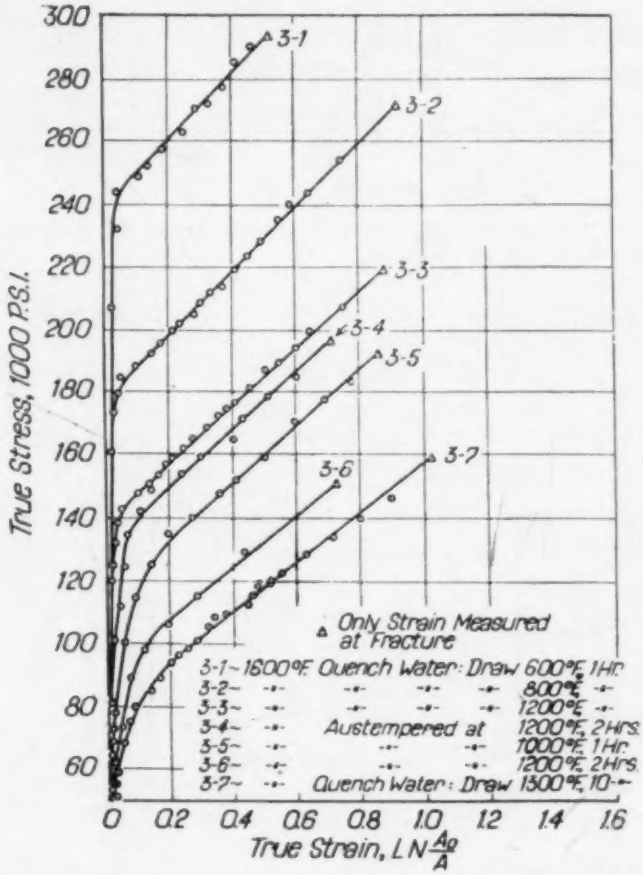


**Fig. 5—True-Stress Versus True-Strain for Different Heat Treatments. Steel No. 3 (S.A.E. 1045).**

results of the tension tests upon them are presented in Fig. 5. Since samples of this steel were both austempered and quenched and drawn; pearlitic, bainitic, and spheroidal structures are represented in the tests. (See Table I for observed microstructures.) The true-stress true-strain curves are very similar for all the heat treatments for each of the two steels. For the specimens of low strength the stress-strain curves show a slight tendency to decrease with increasing strain at large values of the strain. Such large strains are not obtained from specimens heat treated so as to produce high strength.

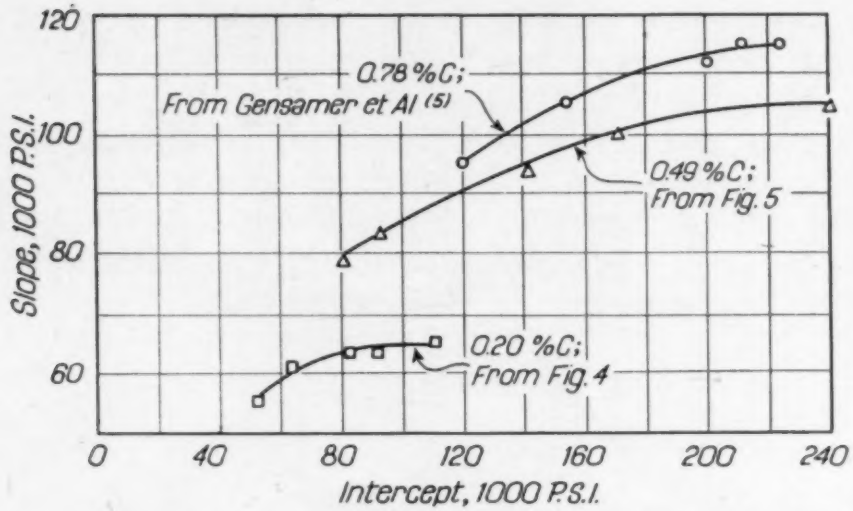


Fig. 6—Rate of Increase of Strength with Strain for Several Steels as a Function of Heat Treatment.

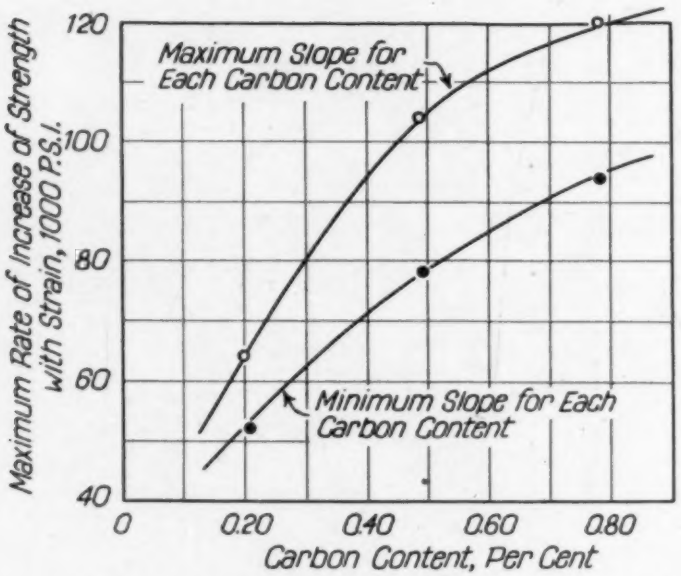


Fig. 7—Rate of Increase of Strength with Strain Versus Carbon Content. (From Fig. 6).

The increase in strength with strain during the plastic deformation is due to work hardening and the rate of work hardening increases slightly as the strength increases for the steels tested. This increase for 3 steels (0.78 per cent carbon steel results taken from Gensamer)[5] is illustrated in Fig. 6 in which the slope of the linear portions of the true stress-strain curves is plotted versus the intercept with the axis of zero strain. As the strength intercept increases the slope increases and appears to approach a maximum for a steel of a given carbon

[5]M. Gensamer, et al.: TRANSACTIONS, American Society for Metals, Vol. 30, 1942.

content. Thus the strengthening of steel due to deformation increases as the strength of the steel increases and is greater as the carbon content increases. The maximum value of the rate of work hardening for each of the three steels is plotted as a function of the carbon content in Fig. 7. The 0.20 per cent carbon steel of this plain carbon series has a lower rate of work hardening then the 1.8 per cent nickel, 0.20 per cent carbon of Fig. 3, indicating that the nickel also raises this rate.

The effects of alloying elements on the strength properties of steel particularly in the plastic range may be conveniently studied by determining true-stress true-strain curves as functions of heat treatment. Knowing that the slope of the curves at large deformations is relatively insensitive to structure changes the stress-strain curves may be determined approximately from the intercept of the work hardening curve with the axis of zero strain and its variation with heat treatment. The variation of this intercept with changes in structure and the slope of the curve at large deformations are characteristic of a given steel and may serve as a basis for a more simple and thorough study of the effects of alloying elements on the mechanical properties. Knowing that such a simple even though approximate relationship holds for a given steel a system may be determined after sufficient experimentation whereby the mechanical properties (yield strength, ductility, etc.), of an alloy may be predicted from its composition. By determining two points on the work hardening curve such as the tensile strength and one other point, the slopes of all other curves in the family may be inferred. It is then only necessary to determine the tensile strength as a function of heat treatment to specify the stress-strain curves for the alloy to a close approximation.

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## DISCUSSION

**Written Discussion:** By C. W. MacGregor, professor of applied mechanics, Massachusetts Institute of Technology, Cambridge, Mass.

The author is to be congratulated on his clear picturization of the effects of heat treatment and carbon content on the work hardening properties of steels through the use of true stress-strain curves. As a result of considerable work with the true stress-strain tension test over a number of years, the writer is convinced more than ever that the use of this form of test will enable us to gather together much information of fundamental value which cannot be revealed by the conventional test. A wealth of background and experience has been built up through the years with reference to the conventional test. Time and considerable experimentation will be necessary in order to do the same for the true stress-strain tension test. For this reason the writer hopes that

Lt. Hollomon and his colleagues at the Watertown Arsenal will continue their useful work in this field.

In studies of this sort, we have found it more convenient to use a machine of the hydraulic type which, by adjusting the release valve, allows the pointer to drop back very slowly so that the fracture load can be observed with considerable accuracy. In addition, the representation of ductility[6] through the true uniform strain $\Sigma_u = \log_e \frac{A_o}{A_u}$ and the true local necking strain. $\Sigma_n = \log_e \frac{A_u}{A_b}$ has proved to be of considerable use. In these strain expressions $A_o$, $A_u$ and $A_b$ refer to the cross-sectional areas at the start, at maximum load and at fracture respectively. Since considerable extension occurs in the vicinity of the maximum load, the cross-sectional area $A_u$ can be obtained with reasonable accuracy either by plotting the load P to a large scale vs. the diameter $d$ in the immediate vicinity of $P_{max}$ or by determining the point on the true stress-strain curve where the true stress equals the slope. Tests have demonstrated that the true uniform and local necking strains are affected quite differently by various mechanical and heat treatment conditions.

### Oral Discussion

J. J. KANTER:[7] On this subject of apparatus for measuring true stress-strain curves, it might be of interest here if I describe another method which we had occasion to work with. We became interested in what the effect of strain aging would be on the true stress-strain curves and, in order to make such measurements, it was necessary to work at somewhat elevated temperatures with a furnace surrounding the test bar. We constructed a furnace with windows through which we could get a full view of the breaking section of the test bar. During the straining, series of photographs of the breaking section profile were taken. From those photographs we were able to make the necessary measurements to plot true stress-strain curves.

It might also be of interest in connection with the paper under discussion to point out that strain aging probably plays a very profound role in affecting the slope of the true stress-strain curve and, consequently, the value of the intercept. With certain steels there can be enough strain aging developed by mild elevations of temperature to change the order in which the curves arrange themselves. Many steels possess a definite blue-brittle peak temperature. In terms of true stress-strain diagrams that peak is manifest as inter-changes in the order of the curves. No doubt, in some of the steels that Lt. Hollomon has worked upon a strain aging component might be the explanation of some of the slope and intercept anomalies. To arrive at a fundamental interpretation of what the intercept means, the strain aging effects should be considered. It would be of considerable interest if this work were repeated on a further series of steels comparing both strain aging and non-strain aging varieties.

GODFREY STANIUS:[8] Am I right in understanding that you say the straight

[6] "The Tension Test," *Proceedings*, American Society for Testing Materials, Vol. 40, 1940.
[7] Materials research engineer, Crane Co., Chicago.
[8] Mechanical engineer, Acme Steel Co., Chicago.

portion of the stress-strain curve occurs after the necking-strain has been reached? If so, has there been any study made as to the shape of the stress-strain curve between the yield point and the necking point similar to what you have here presented? It seems to me that this portion of the curve has more practical significance than what occurs after the necking point.

J. D. DUNBAR:[9] I wonder if Lt. Hollomon would care to give us some details on this testing apparatus he has set up.

### Author's Reply

The author would like to express his appreciation to the discussers of this paper for their generous comments. The author is in full agreement with Professor MacGregor. The total uniform strain may, in many cases, be of more significance than the strain to fracture. In deep drawing applications, in particular, the magnitude of the uniform strain is probably the best comparative measure of the relative drawability of metals.

Mr. Kanter has introduced into the discussion the extremely interesting phenomenon of strain-aging. The mechanism of this increase in strain-hardening at slightly elevated temperatures can, with the present state of knowledge, only be surmised. It is not believed, however, that at the temperature and strain rates employed in the experiments reported in this paper, that there were any significant effects of strain-aging. The effects of elevated temperatures on the shape and location of the stress-strain curves require attention, and it is interesting to note that Mr. Kanter is undertaking such experiments.

The initial part of the stress-strain curve is, as Mr. Stanius suggests, of generally more practical significance than that part after necking occurs. Certain general relations have been established for this initial part of the curve and will be the subject of another paper to be published in the near future. From very small strains to strains of about 0.4 (about 35 per cent reduction in area), the stress-strain curves of most metals obey the following relation:

$$S = K(\varepsilon)^m$$

where S is the stress, $\varepsilon$ the strain, K a constant and m a constant which varies from 0.05 to 0.5 (with different metals).

Several questions have been asked by Professor MacGregor and Mr. Dunbar about the machine which is used for the determination of stress-strain curves. A machine which automatically records load-diameter curves has been constructed and is in operation. This apparatus is described in detail in a paper entitled, "Effect of Strain Rate Upon the Plastic Flow of Steel," which will be published in early 1944 in the Journal of Applied Physics.

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[9]Metallurgist, Army Ordnance, Washington, D. C.

# A STUDY OF THE NITRIDING PROCESS
# I. EFFECT OF AMMONIA DISSOCIATION ON CASE DEPTH AND STRUCTURE

By Carl F. Floe

*Abstract*

*Depth-hardness characteristics and microstructures were determined for nitride cases produced at dissociations of ammonia varying from 15 per cent to 85 per cent. Results are shown for different time intervals of nitriding from 5 hours to 100 hours. It was found that for all dissociations up to at least 65 per cent, a white layer, consisting largely of $Fe_2N$, was formed very shortly after nitriding starts. The depth of this white layer decreases with increasing dissociation of ammonia. The total depth of case beneath the white layer for a given time of nitriding was found to be practically the same regardless of the dissociation up to 65 per cent. At 85 per cent dissociation very little white layer is produced and the depth of case for a given time of nitriding is inferior. By first nitriding at 30 per cent dissociation for a short period, the dissociation may be allowed to increase to as high as 85 per cent with no sacrifice in case depth. Cases finished at 85 per cent have practically no white layer.*

*A considerable saving in ammonia may be effected by nitriding at high dissociations. If this is done, care must be taken to avoid any "dead" zones in the container in which the dissociation may become too high for effective nitriding. Such a condition can be prevented by providing for thorough circulation of the gas.*

## Introduction

THE nitriding process for the surface hardening of steel has increased in importance very rapidly in the last 10 years. The process consists of heating steels of special composition in contact with ammonia gas, usually at temperatures between 925 and 975 degrees Fahr. (495 and 525 degrees Cent.), for periods which vary from 10 to 100 hours depending upon the depth of case desired.

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During this period nitrogen is absorbed, which forms nitrides with the special elements present in the steel, usually aluminum, chromium and molybdenum. These nitrides are precipitated, at the nitriding temperature, along the crystal planes of the iron, which results in the production of an extremely hard and wear resistant case. Iron nitrides are also formed.

Nitriding has been the object of a considerable amount of study which has resulted in a fairly good understanding of the mechanism by which surface hardening takes place. However, very little has been done in the way of a systematic study of the differences in the character of cases produced under different nitriding conditions. This paper presents the results of some experiments in nitriding under very closely controlled conditions with particular reference to the types of cases produced with different degrees of dissociation of ammonia.

## Description of the Process

For a general review of the methods, materials and equipment used in surface hardening by nitriding, the reader is referred to a paper by Homerberg (1).[1] A summary of the early work is contained in the Nitriding Symposium (2). Very little has been published in the scientific journals in recent years, but an excellent description of the process and a bibliography is contained in a bulletin by Homerberg (3).

When ammonia is heated to the nitriding temperature range between 925 and 975 degrees Fahr., very little dissociation occurs except at surfaces capable of catalyzing its decomposition. Steel has such a surface and therefore during nitriding the following reaction will occur at the gas-solid interface:

$$NH_3 = N^* + 3H^* \qquad (1)$$

It is assumed that the atomic hydrogen thus formed passes immediately to the molecular state. A part of the atomic nitrogen is absorbed by the steel and the balance reacts to form $N_2$ which is inert. Since the life of the atomic nitrogen is short, it is necessary to replenish it by continuously supplying fresh ammonia to the steel surfaces. Thus in nitriding it becomes very important to circulate the ammonia in such a way as to constantly re-supply the active nitrogen on all areas to be hardened.

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

In order to assure a sufficient supply of active nitrogen, it is the usual practice to so regulate the flow of ammonia through the nitriding container as to maintain a concentration of 70 per cent $NH_3$ and 30 per cent $N_2$ plus $H_2$ in the exhaust gas. This is commonly spoken of as maintaining the ammonia dissociation at 30 per cent. Actually, due to the change in volume involved, only 17.7 per cent of the ammonia entering the container is dissociated under these conditions. The balance, or 82.3 per cent, simply circulates through the retort and is wasted. Of the amount which is dissociated, only a very small fraction provides nitrogen which is absorbed by the steel.

It is evident that the greater portion of the ammonia that enters the retort is wasted either by dissociation into molecular nitrogen and hydrogen or by failing to dissociate at all. Since one of the principal costs of the process is the cost of ammonia, it is desirable to study ways in which this large wastage may be reduced. Obviously, one way of doing this would be to dissociate a larger proportion of the ammonia. It therefore becomes important to determine the effect of ammonia concentration upon the character of the nitride case produced.

In general, any nitride case is made up of two separate and distinct zones. The first of these, or outer zone, represents the region in which all nitride forming elements, including iron, have been converted to nitrides. This zone is frequently called the "white layer" since it appears white under the microscope after a nital etch. The second zone beneath the white layer represents the region in which most of the special elements have been converted to nitrides but not the iron. Under normal nitriding conditions the second zone is at least ten times as deep as the first zone.

The outer zone, or white layer, is very brittle and is therefore usually removed by grinding before a nitride case is put into service. In some instances its removal is not considered necessary. The corrosion resistance of the white layer is very good and therefore from this standpoint it is desirable not to remove it.

## Experimental Methods

*Nitriding Apparatus*—A special apparatus was constructed in which it was possible to simultaneously nitride four different specimens, one at 15 per cent dissociation of ammonia, one at 30 per cent,

one at 45 per cent and one at 65 per cent respectively. Separate runs were also made at 85 per cent dissociation. This apparatus, a diagram of which is shown in Fig. 1, consists of four different nitriding chambers made from Pyrex glass tubing, each chamber being about 1.5 inches in diameter and 30 inches long. The top of each chamber was sealed with a rubber stopper, from which the specimen to be nitrided was suspended by a nickel wire. The four

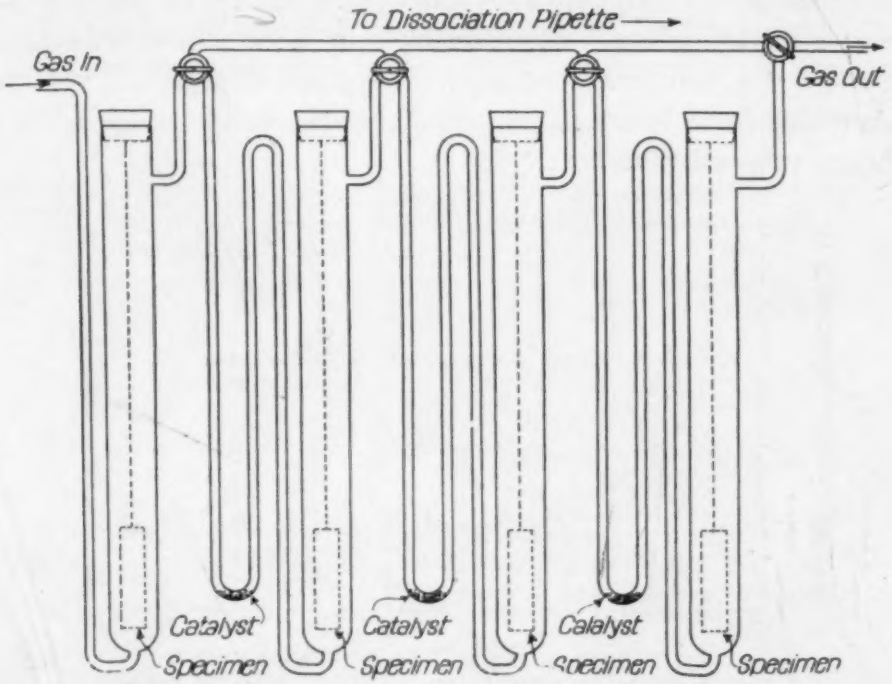


Fig. 1—Diagram of Apparatus Used for Simultaneously Nitriding Specimens at Different Degrees of Dissociation of Ammonia.

chambers were connected by the U-tubes as shown. A special catalyst for cracking the ammonia was placed in the bottom of each U-tube, the amount added being determined by the dissociation required in the adjacent nitriding chamber.

The ammonia entered the first nitriding chamber on the left of the diagram through the tube as shown. By placing some catalyst in this tube and by regulating the flow of ammonia, the dissociation in the first nitriding chamber could be controlled at 15 per cent. The exit gas passed from the first chamber, through a second U-tube containing more catalyst, into the second nitriding chamber. The dissociation in this tube was controlled at 30 per cent. Similarly, the exit gas from the second nitriding chamber passed on through the third and fourth chambers in which the dissociation was controlled at 45 and 65 per cent respectively.

The four interconnected nitriding chambers and dissociation tubes were placed in a Lindberg Cyclone tempering furnace in such a way that the suspended specimens could be simultaneously heated to the nitriding temperature of 975 degrees Fahr. (525 degrees Cent.). This temperature was checked by placing a thermocouple in each chamber. The U-tubes were connected through stopcocks in a manner that made it possible to check the dissociation of ammonia in each chamber at frequent intervals by means of a standard pipette. During a nitriding cycle the variation in dissociation was seldom more than $\pm 1$ per cent. At each dissociation, separate specimens were nitrided for 5 hours, 10 hours, 20 hours, 36 hours, 60 hours and 100 hours respectively.

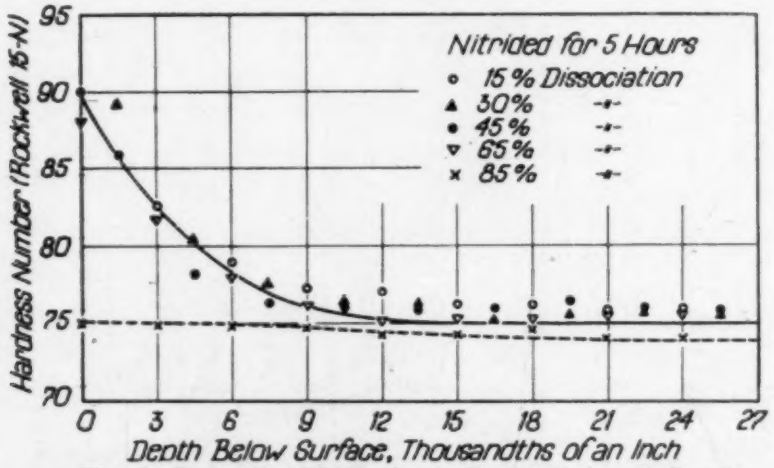


Fig. 2—Rockwell 15N Hardness Characteristics of Samples Nitrided for 5 Hours at the Dissociations of Ammonia Shown.

*Steel Used*—Depth-hardness specimens, ½ inch square and 4 inches long, were machined from ⅞-inch round Nitralloy 135. Before machining, the stock was heat treated by quenching in oil from 1725 degrees Fahr. (940 degrees Cent.) and tempering at 1250 degrees Fahr. (675 degrees Cent.) for 2 hours. Opposite surfaces of the specimens were ground parallel on a surface grinder.

After nitriding, the specimens were taper ground to 0.015 inch per inch of length in order to make depth-hardness determinations. Both Rockwell 15N and Vickers (10 kg. load) hardness readings were taken.

The composition of the steel used was as follows:

| | | | |
|---|---|---|---|
| C | 0.34 per cent | Cr | 1.30 per cent |
| Mn | 0.55 per cent | Al | 1.24 per cent |
| Si | 0.25 per cent | Mo | 0.17 per cent |

*Preparation of Photomicrographs*—Standard methods were used in the preparation of all photomicrographs. However, it was necessary to mount each sample in a special steel clamp in order to preserve a sharp edge in polishing. In this way the true depth of the white layer on each sample was revealed.

## Data and Results

*Depth-Hardness Curves*—Figs. 2 to 7 inclusive show the results of depth-hardness determinations on cases produced at the several

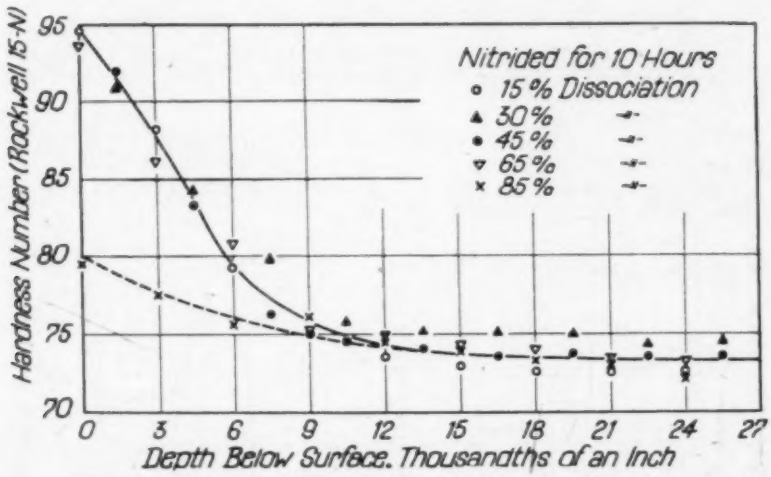


**Fig. 3—Rockwell 15N Hardness Characteristics of Samples Nitrided for 10 Hours at the Dissociations of Ammonia Shown.**

dissociations of ammonia and the varying time intervals of nitriding. It is evident from an inspection of the data plotted that for a given period of time there is very little difference in the depth-hardness characteristics for dissociations between 15 and 65 per cent. However, at 85 per cent the cases are distinctly more shallow, indicating that at this dissociation nitriding is very slow.

A similar set of curves in which the Vickers-Brinell hardness is plotted against the depth below the surface in inches is given in Figs. 8 to 13 inclusive. The results agree with those obtained for the Rockwell 15N hardness in that they show that there is very little difference in the depth-hardness characteristics of cases produced by varying the ammonia dissociation from 15 to 65 per cent.

The scatter in the hardness readings shown in Figs. 2 to 13 inclusive may be partially explained by the fact that the value obtained in any given instance is a function not only of the actual hardness and depth of case beneath the indentor, but also its brittleness. As will

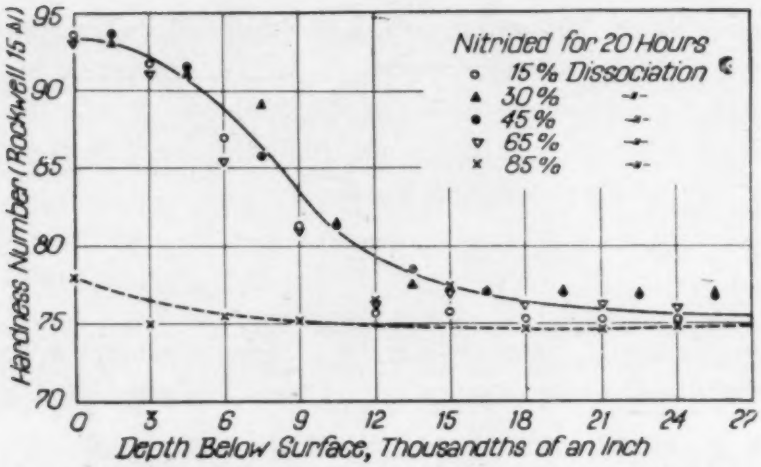


**Fig. 4—Rockwell 15N Hardness Characteristics of Samples Nitrided for 20 Hours at the Dissociations of Ammonia Shown.**

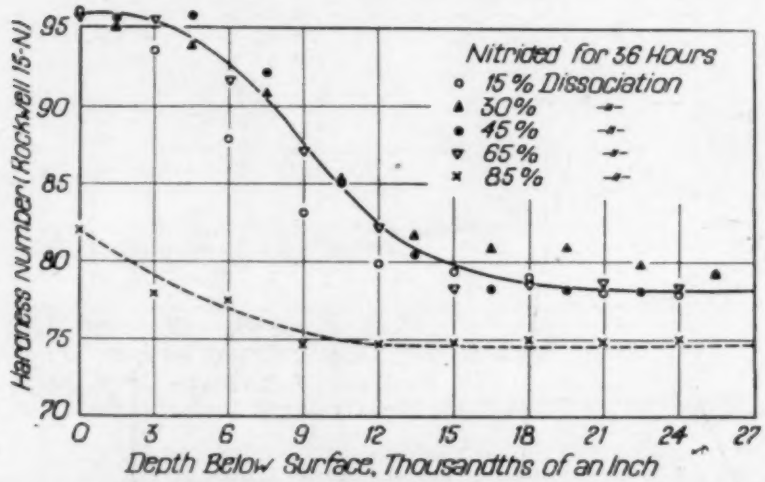


**Fig. 5—Rockwell 15N Hardness Characteristics of Samples Nitrided for 36 Hours at the Dissociations of Ammonia Shown.**

be shown later, it appears that the brittleness factor, which is a function of the depth of white layer, varies to a certain extent with the dissociation of ammonia which existed when the case was formed.

*Typical Case Structures*—Photomicrographs at × 500 of the cases produced at different dissociations of ammonia and different nitriding periods are shown in Figs. 14 to 19 inclusive. Photomicrographs were also taken at × 100, which are not included, but which showed that there was very little difference in the total depth of case produced in a given time interval at the different dissociations of ammonia within the range 15 to 65 per cent. This substantiates the results of the depth-hardness measurements.

Examination of the photomicrographs further shows that the tendency to form a heavy white layer decreases with increasing

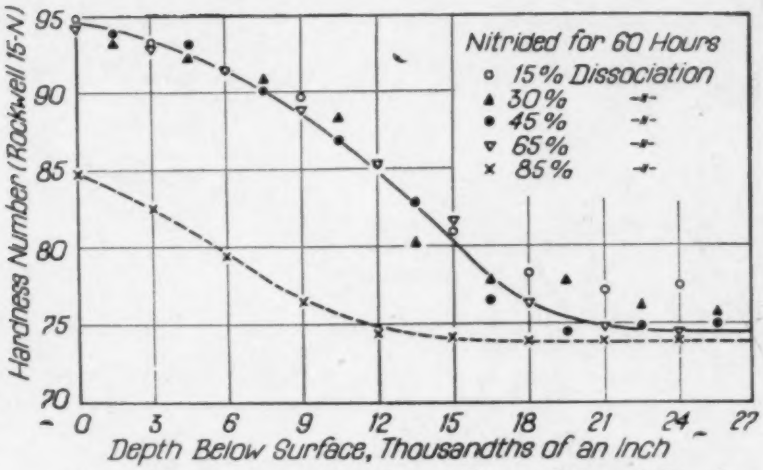


**Fig. 6—Rockwell 15N Hardness Characteristics of Samples Nitrided for 60 Hours at the Dissociations of Ammonia Shown.**

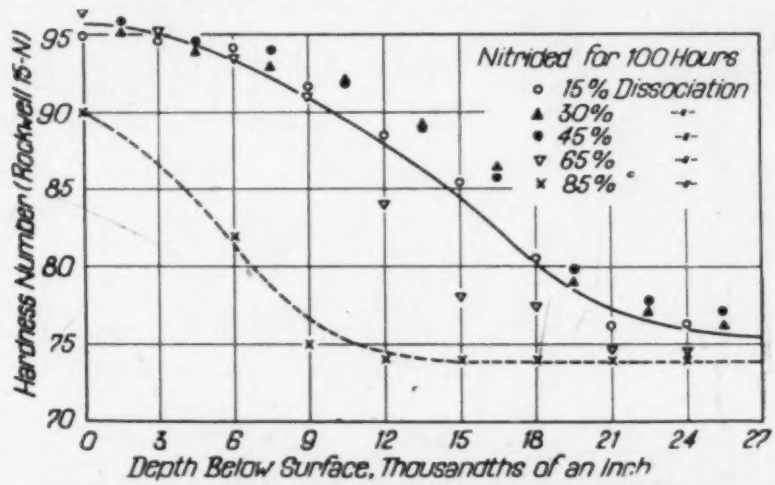


**Fig. 7—Rockwell 15N Hardness Characteristics of Samples Nitrided for 100 Hours at the Dissociations of Ammonia Shown.**

dissociation of ammonia. However, it should be observed that a thin white layer is formed even in 5 hours at 65 per cent dissociation. It was previously thought that the white layer was not formed except after comparatively long periods of nitriding. The reason for this belief is that these thin white layers are not ordinarily observed unless the samples are polished between clamps.

Photomicrographs of the samples nitrided at 85 per cent dissociation are not included as very little case was produced. No white layer was observed even after nitriding for 100 hours.

*Large Scale Nitriding Run*—To check the results of nitriding at different degrees of dissociation of ammonia on a scale more nearly approaching the commercial, two Lindberg nitriding furnaces with containers approximately 8 inches in diameter and 10 inches deep

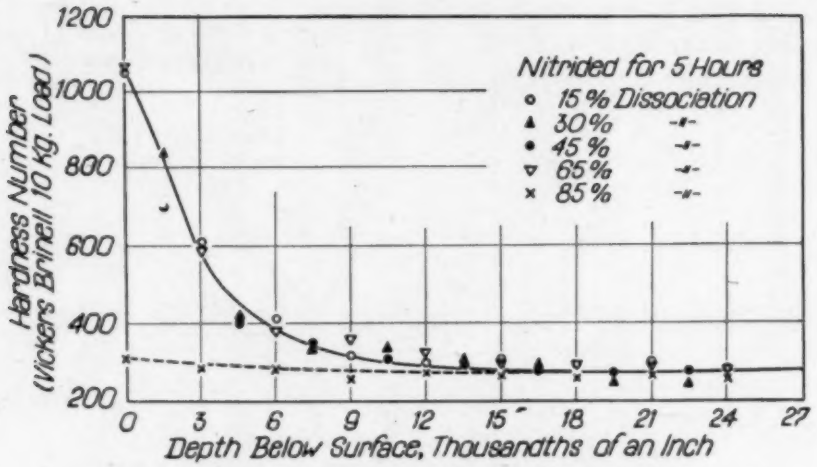


Fig. 8—Vickers-Brinell Depth-Hardness Characteristics for Samples Nitrided for 5 Hours at the Dissociations of Ammonia Shown.

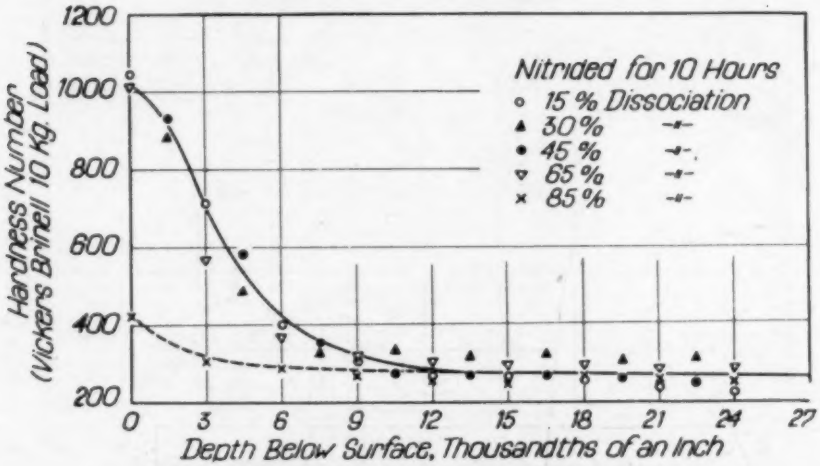


Fig. 9—Vickers-Brinell Depth-Hardness Characteristics for Samples Nitrided for 10 Hours at the Dissociations of Ammonia Shown.

were loaded with small pieces of Nitralloy. A depth-hardness specimen was placed in the center of each charge. The flow of ammonia through the first furnace was regulated to give a dissociation of 30 per cent. The exhaust gas from this furnace was passed through the second furnace in which the ammonia dissociation was maintained at 65 per cent. Nitriding was carried out for 60 hours at 975 degrees Fahr. (525 degrees Cent.). Photomicrographs of the resultant cases at $\times$ 100 and $\times$ 500 are shown in Fig. 20. It may be seen that the sample nitrided at 65 per cent dissociation has approximately the same depth of case but much less white layer than the sample nitrided at 30 per cent dissociation. This confirms the previous results. The depth-hardness characteristics of the two samples were also very similar and agree closely with the values shown in Figs. 6 and 12.

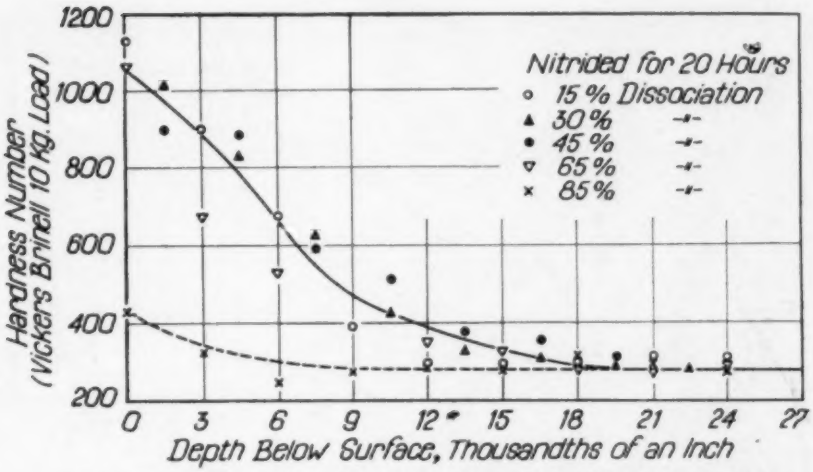


Fig. 10—Vickers-Brinell Depth-Hardness Characteristics for Samples Nitrided for 20 Hours at the Dissociations of Ammonia Shown.

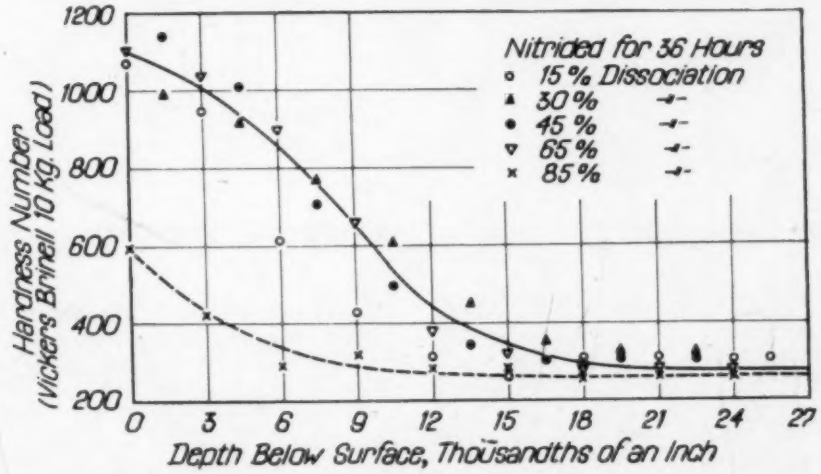


Fig. 11—Vickers-Brinell Depth-Hardness Characteristics for Samples Nitrided for 36 Hours at the Dissociations of Ammonia Shown.

*Nitriding at Low and High Ammonia Dissociations*—From the above results it appears that the principal difference between cases produced at different degrees of dissociation of ammonia is the depth of white layer formed, lower degrees of dissociation producing deeper white layers. It may then be concluded that the white layer will be established more rapidly at the beginning of a heat if the dissociation is first kept low. It may therefore be advantageous to first nitride at low degrees of dissociation. To check this, the following experiment was made: Three depth-hardness samples were first nitrided for 10 hours at 30 per cent dissociation. No. 1 was next nitrided for 90 hours at 45 per cent dissociation; No. 2, 90 hours at 65 per cent dissociation; and No. 3, 90 hours at 85 per cent dissociation. The results of depth-hardness measurements are shown in Fig. 21 and

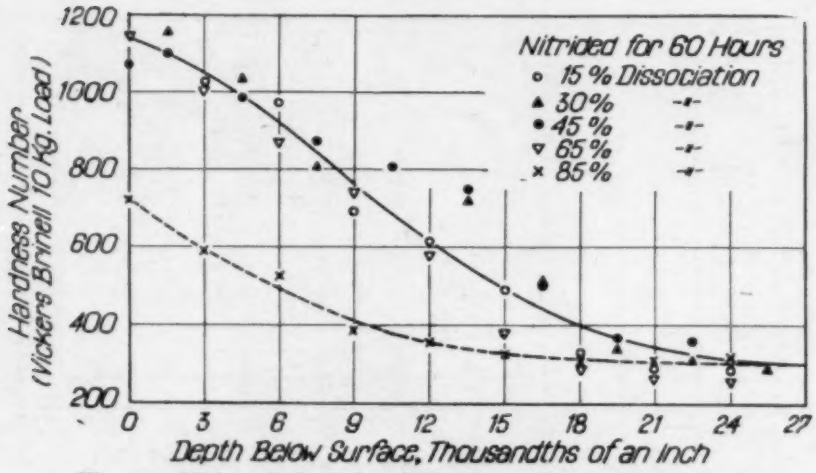


Fig. 12—Vickers-Brinell Depth-Hardness Characteristics for Samples Nitrided for 60 Hours at the Dissociations of Ammonia Shown.

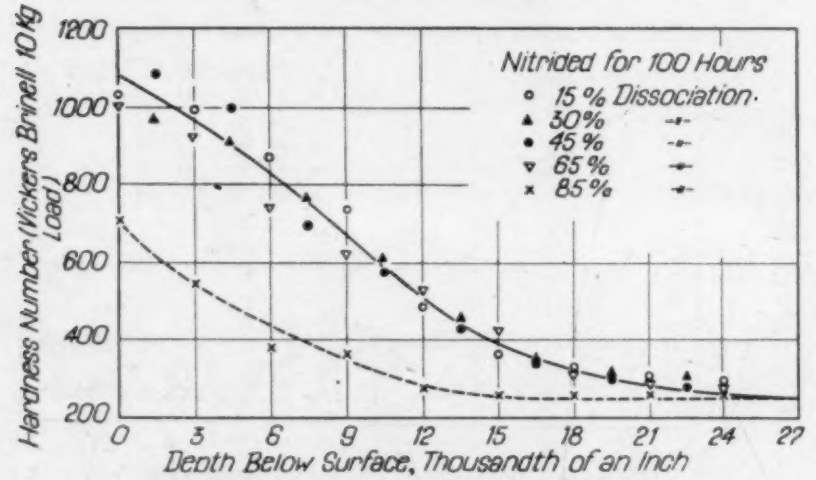


Fig. 13—Vickers-Brinell Depth-Hardness Characteristics for Samples Nitrided for 100 Hours at the Dissociations of Ammonia Shown.

photomicrographs in Fig. 22. The depth-hardness curves indicate a little better result for the sample finished at 45 per cent. However, the photomicrographs show a heavy white layer for this sample and practically no white layer for the sample finished at 85 per cent. When it is considered that the white layer is usually not desirable, the advantage of greater case depth in Sample No. 1 no longer exists to any great extent. The conclusion is that there are advantages in first nitriding at low ammonia dissociations, followed by allowing the dissociation to increase to as high as 85 per cent. In this way a very much greater proportion of the ammonia will be utilized and better case structures will be produced. Table I shows the amount of ammonia wasted when operating at various degrees of dissociation. It may be seen that at 65 per cent dissociation three times as much of the total ammonia is utilized as at 30 per cent.

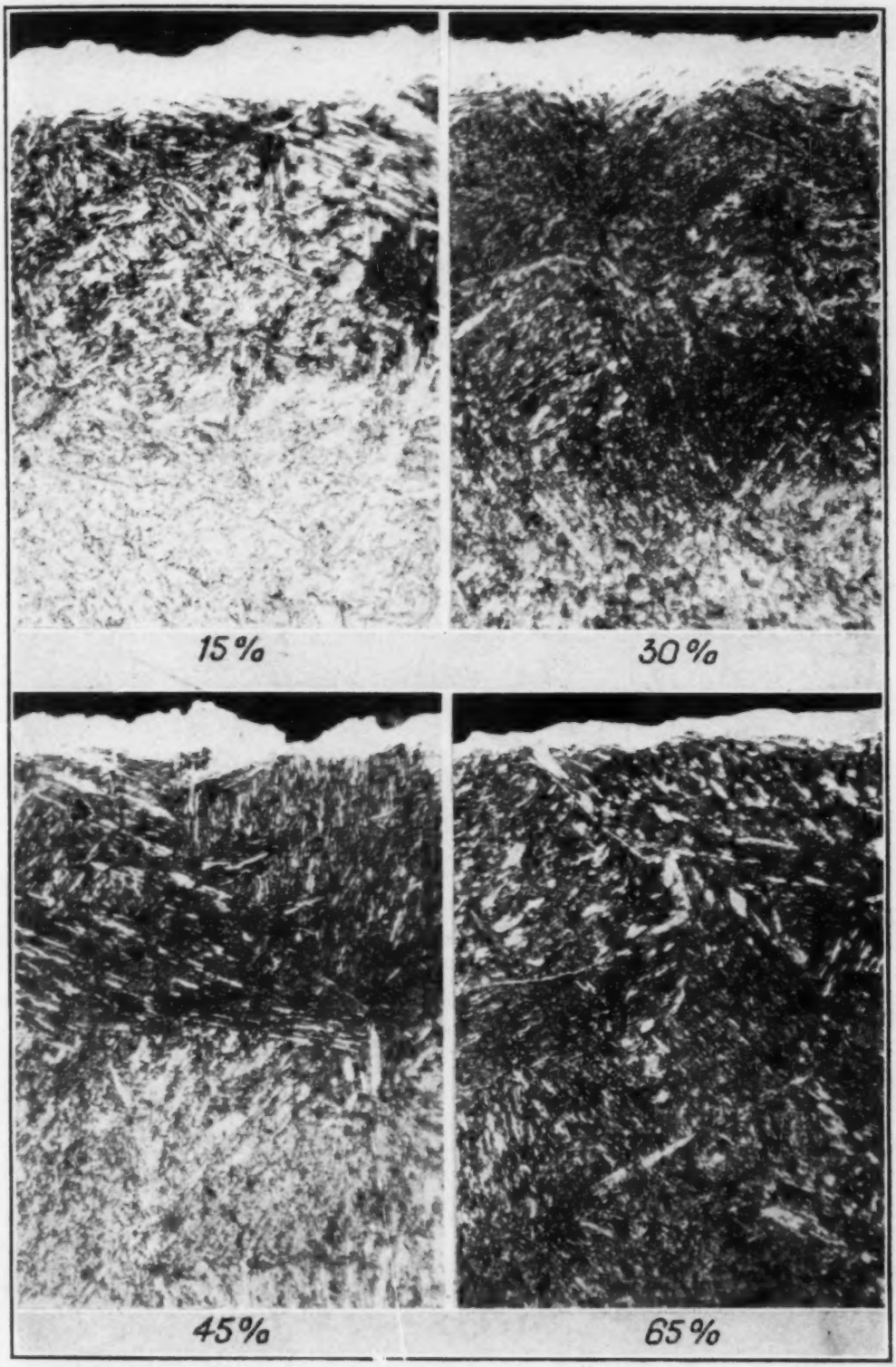


Fig. 14—Typical Case Structures Produced by Nitriding for 5 Hours at the Ammonia Dissociations Shown. × 500.

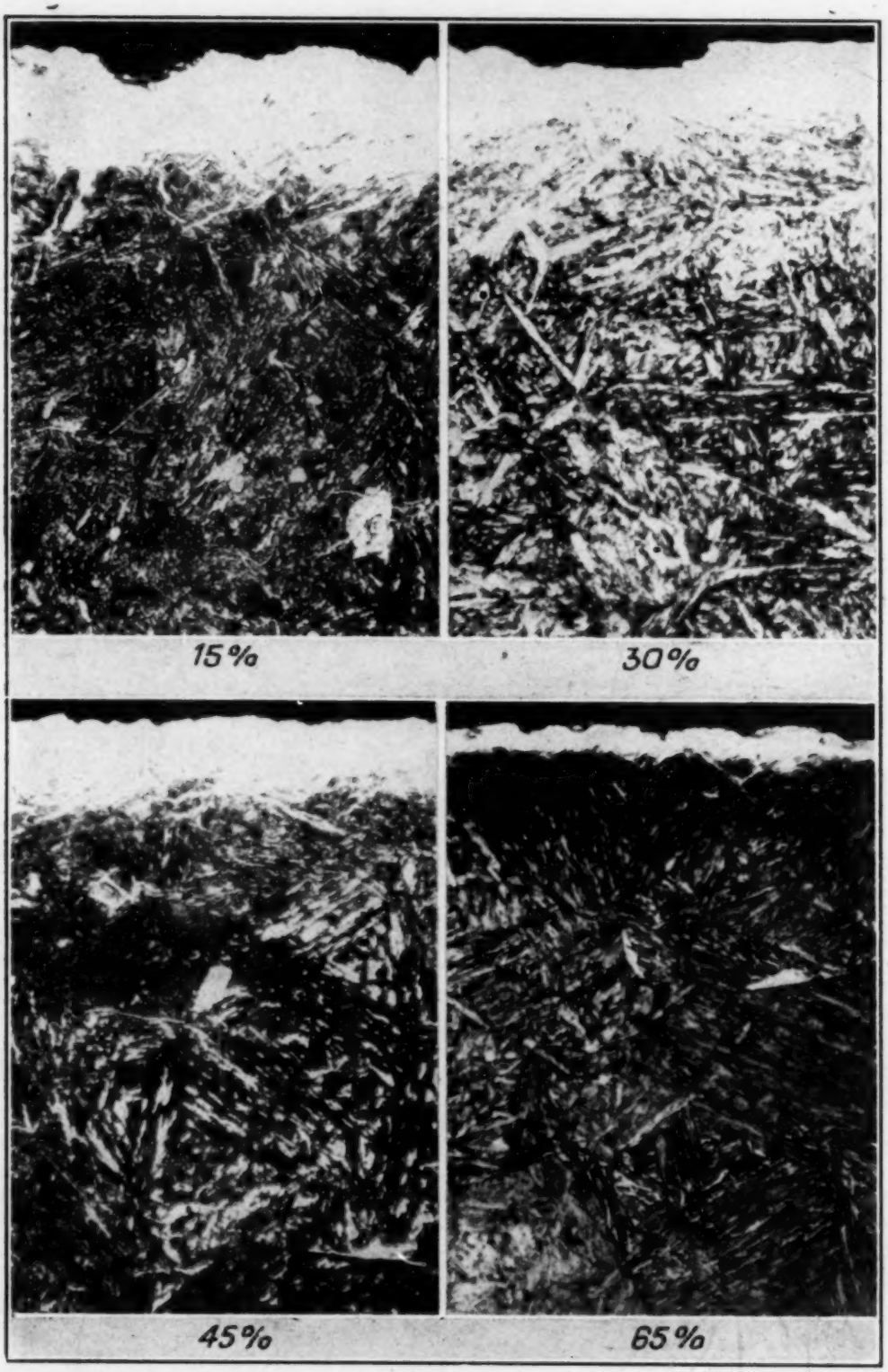


Fig. 15—Typical Case Structures Produced by Nitriding for 10 Hours at the Ammonia Dissociations Shown. × 500.

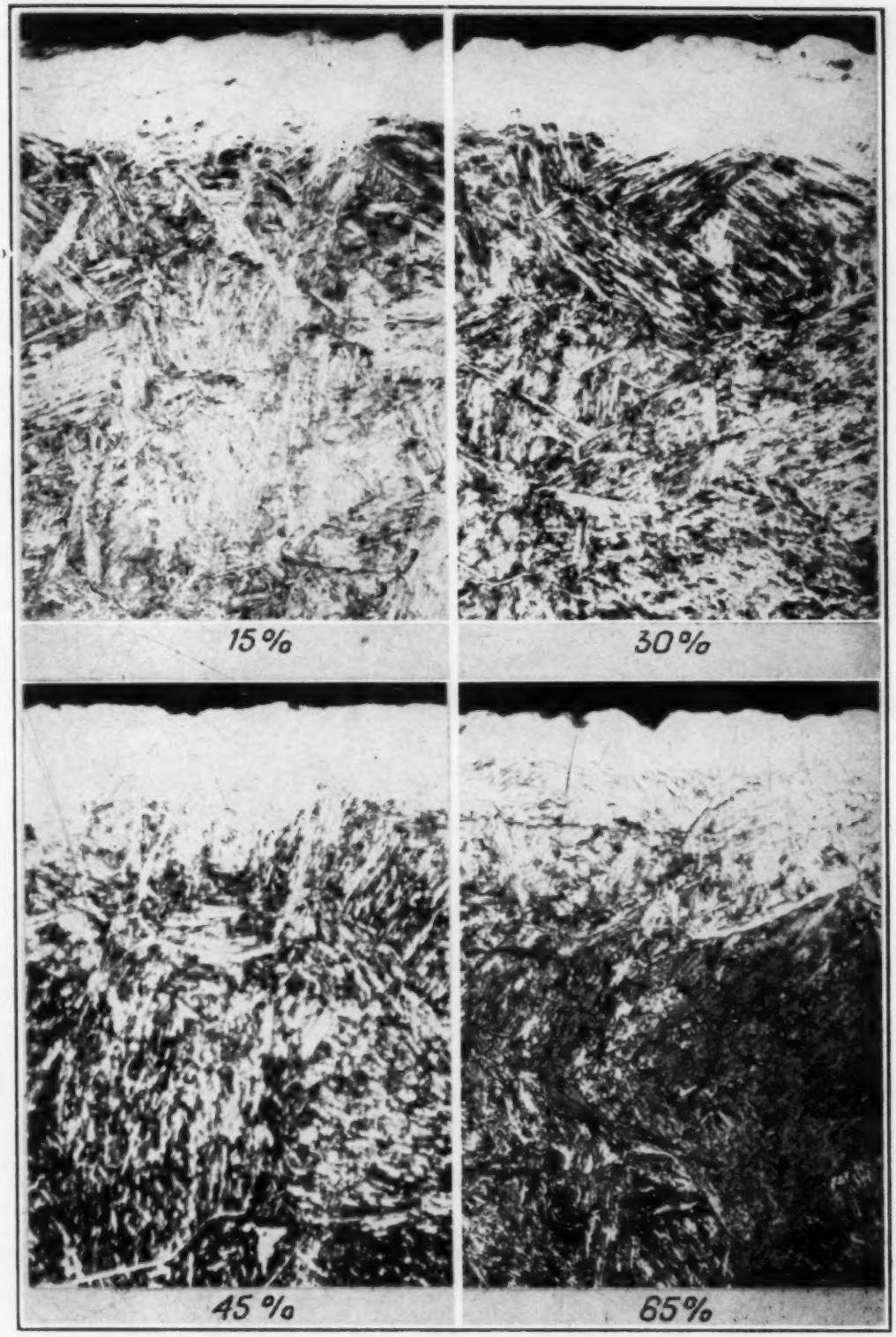


Fig. 16—Typical Case Structures Produced by Nitriding for 20 Hours at the Ammonia Dissociations Shown. × 500.

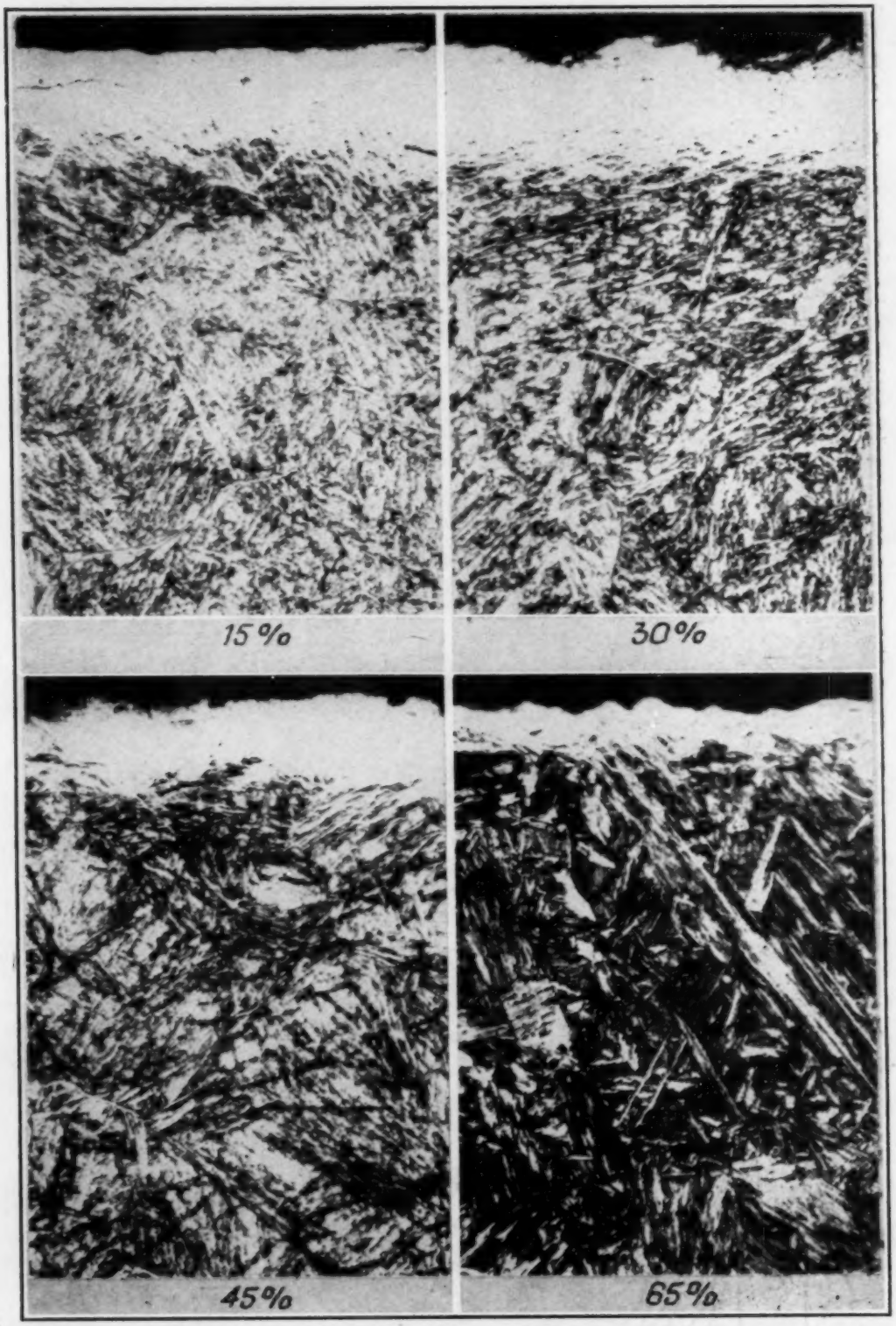


Fig. 17—Typical Case Structures Produced by Nitriding for 36 Hours at the Ammonia Dissociations Shown. × 500.

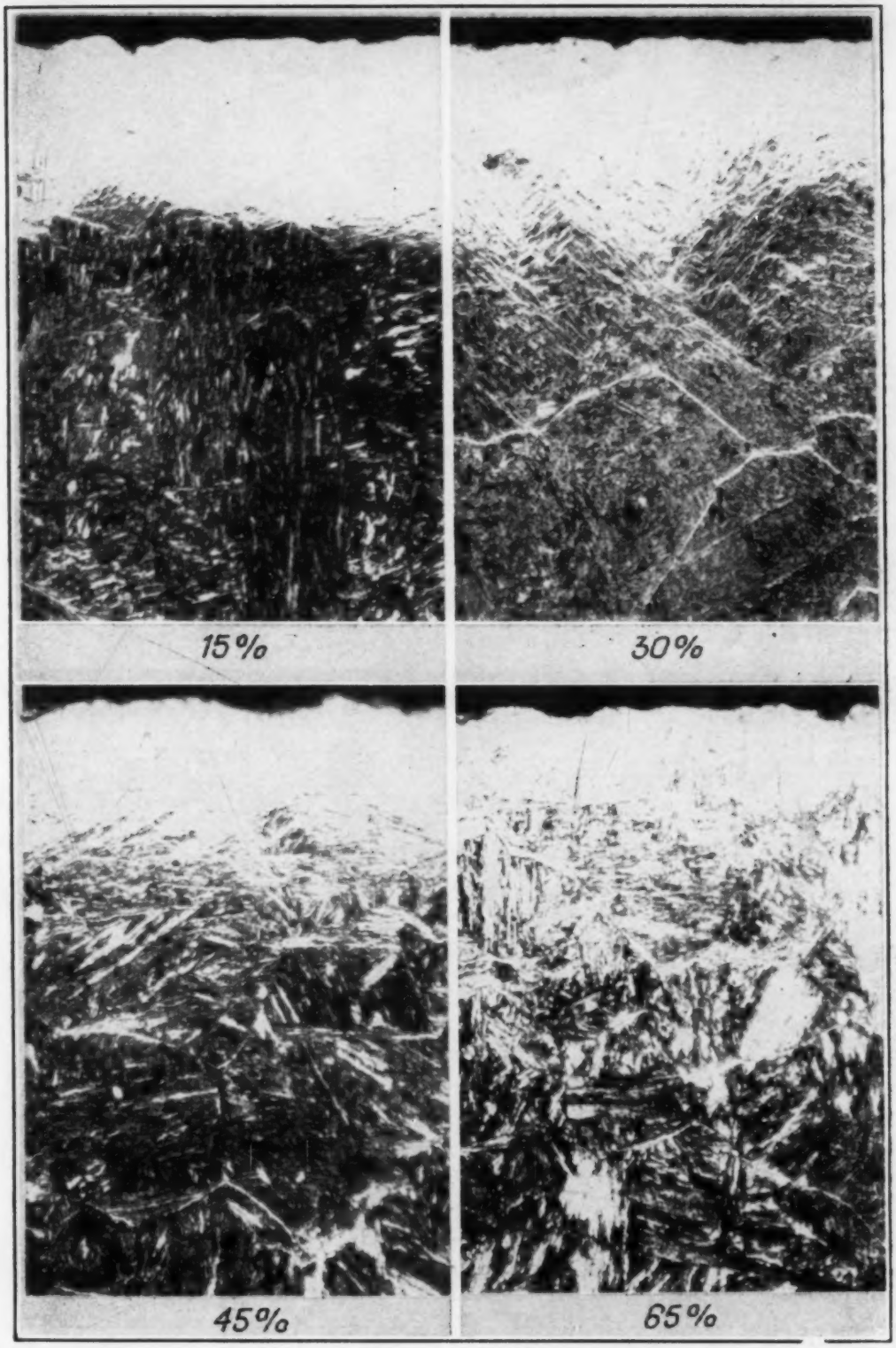


Fig. 18—Typical Case Structures Produced by Nitriding for 60 Hours at the Ammonia Dissociations Shown. × 500.

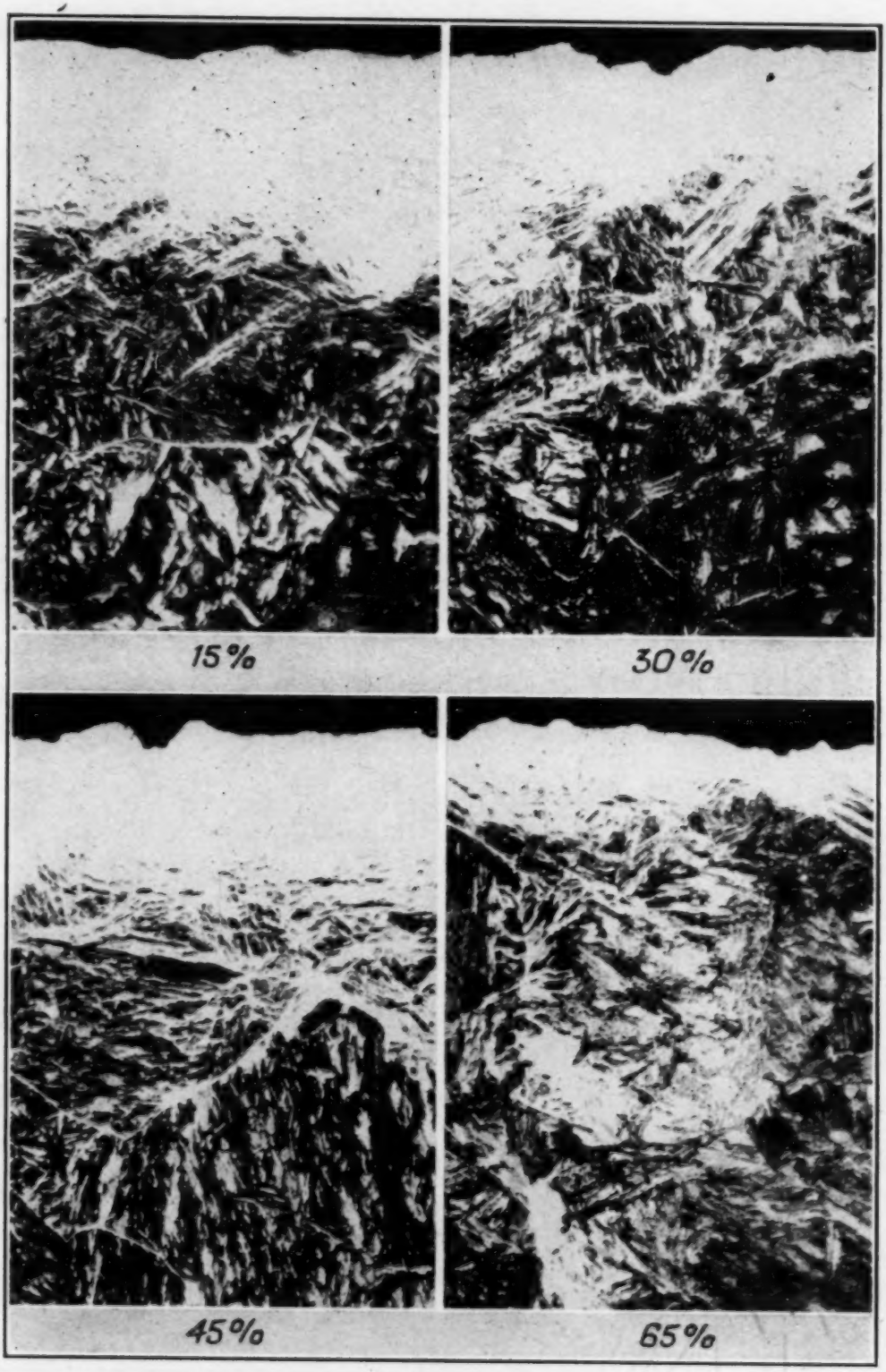


Fig. 19—Typical Case Structures Produced by Nitriding for 100 Hours at the Ammonia Dissociations Shown. × 500.

**Table I**
**Analysis of Exit Gases and Percentages of Ammonia Wasted for Various Dissociations of Ammonia in Nitriding**

| Per Cent Dissociation of Ammonia | Analysis of Exit Gas Per Cent by Volume | | | Per Cent Ammonia Wasted |
|---|---|---|---|---|
| | $NH_3$ | $N_2$ | $H_2$ | |
| 15 | 85.0 | 3.75 | 11.25 | 91.9 |
| 30 | 70.0 | 7.5 | 22.5 | 82.3 |
| 45 | 55.0 | 11.25 | 33.75 | 71.0 |
| 65 | 35.0 | 16.25 | 48.75 | 51.9 |
| 85 | 15.0 | 21.25 | 63.75 | 26.1 |

## Discussion of Results

It has been demonstrated that nitriding can be successfully carried out using dissociations of ammonia as high as 65 per cent and that up to this point the case characteristics actually improve with increasing dissociation due to a decreasing tendency to form a heavy white layer. It has further been shown that if nitriding is first carried out at 30 per cent dissociation for a short period, the balance of the cycle can be completed at dissociations as high as 85 per cent.

The danger of using such high dissociations in commercial practice is that uniformity of gas composition does not ordinarily exist in all parts of the nitriding container. "Dead" zones are apt to form in which the dissociation becomes very high, while in other zones where the gas flow is more rapid, the dissociation will be lower. At points near the ammonia inlets it will be less than at points near the exits, although the difference in this case will also depend upon any auxiliary circulation employed, such as fans. It is of course the average dissociation over the entire container that is measured. The effect of the formation of zones in which the dissociation becomes as high as 85 per cent or higher may be to produce soft surfaces on the parts occupying these zones. This would be particularly true if the dissociation exceeded 85 per cent during the entire cycle. It is obvious that the reason it has been found that a dissociation of 30 per cent will consistently give good results in commercial nitriding is that under these conditions it is practically certain that in no zone of the furnace will the dissociation exceed the percentage that will give a good nitrided case. This reason for the necessity of maintaining the dissociation at 30 per cent has not been previously recognized.

The reason that the total depth of nitrided case produced is largely independent of the ammonia dissociation up to above 65

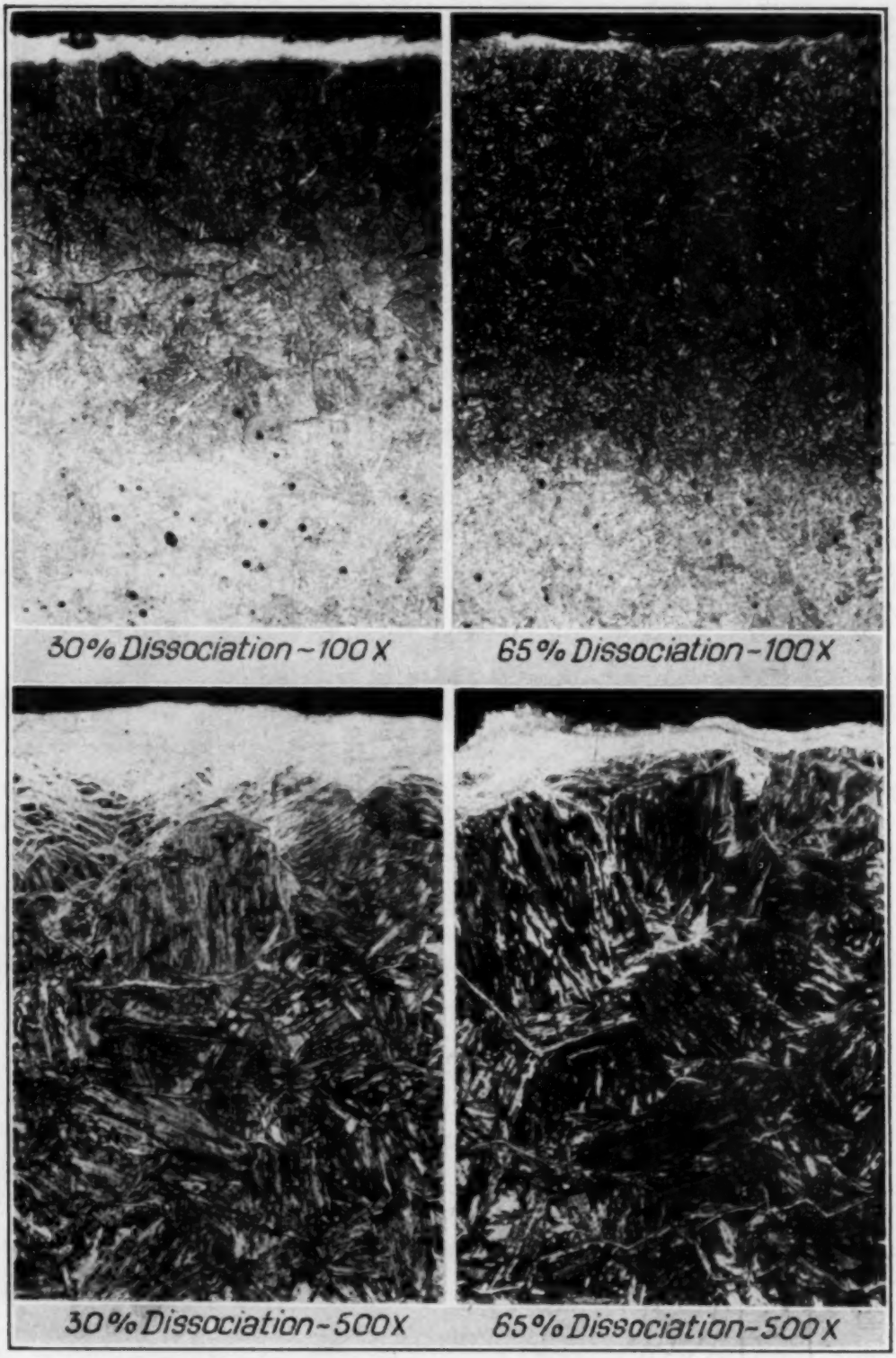


Fig. 20—Structure of Case Produced by Nitriding with Two Furnaces in Series, One Furnace at 30 Per Cent Dissociation and the Other Furnace at 65 Per Cent Dissociation.

per cent is evident from an examination of the photomicrographs. Up to this percentage a thin white layer is formed on the surface of the steel very soon after nitriding is started. As previously discussed, this layer is considered to be largely $Fe_2N$ plus $Fe_4N$. Once formed, the depth of nitride case produced becomes only a function of the rate of diffusion of nitrogen from this layer into the steel beneath. The depth of case beneath the white layer therefore becomes independent of the gas composition, the only condition being that there must be sufficient ammonia present to prevent the de-

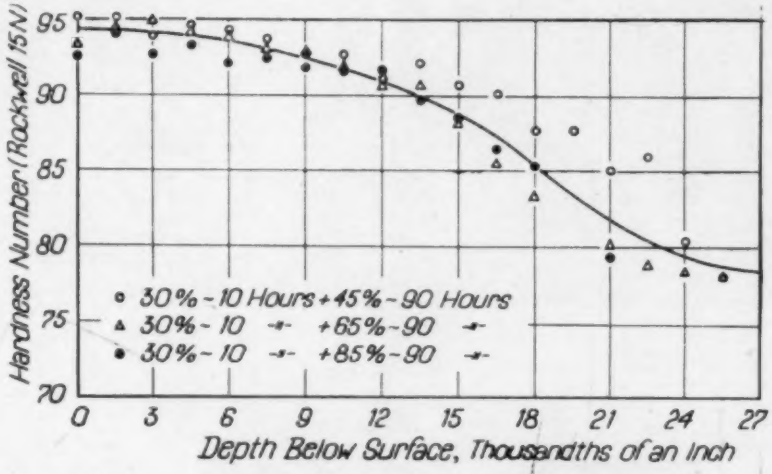


**Fig. 21—Rockwell 15N Depth-Hardness Characteristics for Samples Nitrided at Two Different Dissociations of Ammonia as Shown.**

composition of the $Fe_2N$. The only effect of increasing the ammonia concentration beyond this point is to increase the depth of white layer. There is no advantage in this method of increasing case depth since in most instances the white layer must be ground off after nitriding. In many instances, particularly where sharp corners exist in the work, it is highly desirable to eliminate the white layer altogether.

From the above considerations it appears that more ideal nitriding conditions and better utilization of the ammonia may be obtained in several ways. It is evident that mechanical means of circulation of the gas within the retort will provide more uniform nitriding conditions over all surfaces than will be obtained by simply allowing the ammonia to enter the container at the bottom and be exhausted at the top. A furnace which will allow nitriding to be carried out at high dissociations of ammonia must necessarily be designed in such a way as to provide a system of gas circulation

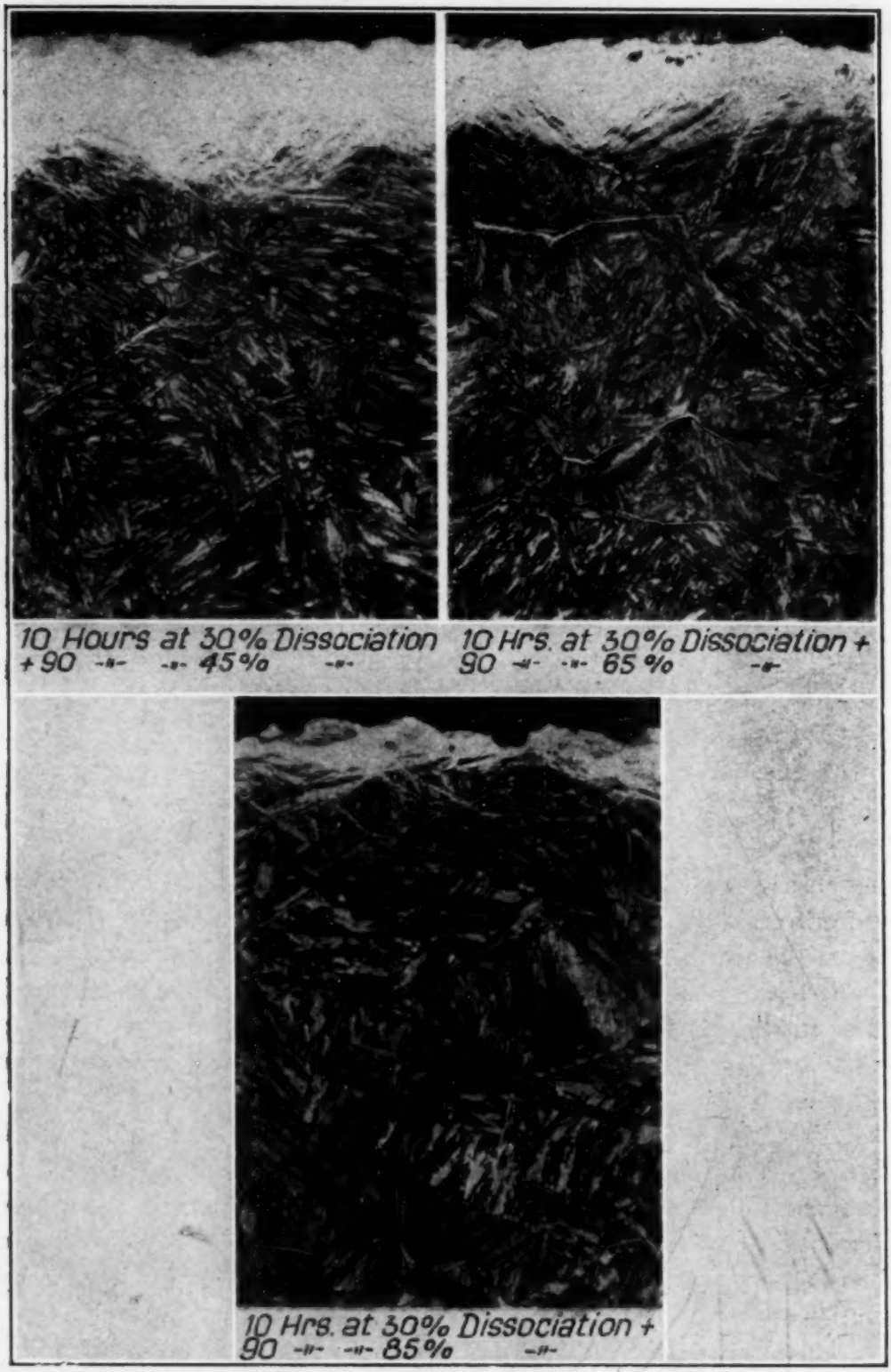


**Fig. 22—Structure of Case Produced by First Nitriding Samples for 10 Hours at 30 Per Cent Dissociation, Followed by Nitriding for 90 Hours at 45, 65 and 85 Per Cent Dissociation Respectively. × 500.**

that prevents any great differences in the degree of dissociation in different parts of the retort. Such a furnace would also have the great advantage of producing cases of uniform structure on all parts and make it possible to nitride under such conditions that practically no white layer would be formed.

Recirculation of the exit gas is another method for utilizing more of the ammonia. If used on a single furnace, it would be necessary to bleed in fresh ammonia on the inlet side and bleed off a corresponding portion of the exhaust gas on the exit side. The dissociation could be maintained at a maximum of less than 85 per cent, and sufficient gas recirculated to insure that no dead zones would exist in the container. The cooling effect of the recirculation would of course have to be taken into consideration. Furnaces can be constructed in such a way that the recirculated gas never leaves the heating chamber. If several furnaces are used it may be more advantageous to pass the gas from one furnace to another. A logical method would be to maintain a low dissociation (30 per cent) in the last furnace to be loaded and pass the gas from this furnace into successive furnaces in the order of decreasing lengths of time necessary to complete the nitriding cycle in each.

It is a well known fact that the rate of ammonia dissociation increases with time during a given nitriding cycle. The reason for this appears to be that the white layer is capable of breaking down the ammonia at a more rapid rate than the original steel surfaces. This means that in most instances it is necessary to increase the rate of flow of ammonia during a nitriding cycle if the dissociation is to be maintained at 30 per cent. However, the results reported here show that if nitriding is started at 30 per cent dissociation, this percentage may be allowed to increase with time without danger of producing inferior cases.

Since this paper has been largely concerned with decreasing the amount of ammonia used in nitriding, it is desirable to list briefly all of the factors which affect ammonia consumption. They are as follows:

1. The percentage of the total ammonia that is allowed to dissociate.
2. The time of nitriding.
3. The surface area of the parts being nitrided.
4. The amount of ammonia dissociated by the walls of the

container, fixtures and heated portions of inlet and exhaust tubes.

5. The rate of ammonia dissociation, which is controlled by:
   a. Temperature.
   b. Nature of surfaces being nitrided.
   c. Rate of gas circulation.

## Summary and Conclusions

From the results obtained the following conclusions may be drawn:

1. The depth-hardness characteristics of nitride cases produced at dissociations of ammonia varying from 15 to 65 per cent are very similar. At 85 per cent dissociation the depth-hardness characteristics are decidedly inferior.

2. A white layer, consisting largely of $Fe_2N$, is formed on nitride cases very shortly after nitriding is started if the ammonia dissociation is less than 65 per cent.

3. The depth of white layer formed decreases with increasing dissociation of ammonia. The total depth of case beneath the white layer is the same regardless of the ammonia dissociation up to 65 per cent.

4. If nitriding is first carried out at 30 per cent dissociation for a short period, the dissociation may be allowed to increase to as high as 85 per cent with no sacrifice in case depth. Cases finished at 85 per cent dissociation will have practically no white layer.

5. A considerable saving of ammonia can be effected by nitriding at high dissociations. However, if this is done, it is necessary to insure against "dead" zones in the container in which the dissociation may become so high as to prevent effective nitriding. This can best be done by thorough circulation of the gas. Recirculation of a portion of the exhaust gas may accomplish the same purpose.

## Acknowledgments

The author is particularly indebted to: The Nitralloy Corporation of New York City, who provided all funds for carrying out the work; Dr. V. O. Homerberg, for many helpful suggestions and criticisms; and Mr. Joseph Connelly, who performed many of the experiments.

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## DISCUSSION

**Written Discussion:** By Herman H. Hanink, laboratory supervisor, Wright Aeronautical Corp., Paterson, N. J.

The practical value of this paper is obvious, especially to those concerned with the nitriding of parts requiring removal of the white layer for proper operation or parts requiring sharp corners. A part in the latter category is illustrated (Fig. A) to show the type of corner chipping encountered with even the most careful shop handling. As shown in Fig. B, this chipping extends only through the white layer.

We have used a high dissociation in production nitriding as a partially successful means of controlling the chipping of parts such as the one illustrated. However, because of the previous absence of any well-defined limitations on dissociation and because of practical difficulty in maintaining a high dissociation, we have been very conservative in this regard.

Under production conditions, unless the area of steel surface exposed for nitriding is rather large, it is difficult to reach over 40 per cent dissociation at any time in the cycle, even with an extremely small flow of fresh ammonia. Passing gas from one furnace to the other might not be much more successful, and would not be compatible with the present necessity of simplifying all heat treating processes. The latter would also serve as an objection to changing from a low to a high dissociation during the course of the cycle. For precise and flexible control of dissociation, independent of furnace loading, pre-dissociation of the ammonia in a separate retort might be a desirable practice.

The danger of using a very high dissociation in commercial practice has been brought out by Dr. Floe. This point should be strongly emphasized. The uniformity with which parts are distributed in the furnace charge has a decided effect on gas circulation, and often is beyond adequate control. Close attention to the condition of enameled retorts and the type of fixtures used is also necessary. We have noted instances where the average dissociation throughout a cycle has not exceeded 40 per cent, but where some parts have partially nitrided or not nitrided at all, due to very high local dissociation as a result of the use of improper supporting fixtures.

In connection with the observed difficulties caused by excessively high local dissociation, it was noted that the ability of a surface to nitride properly under such conditions was dependent on the type of surface finish. Even a slight burnishing appeared to prevent the formation of a case or to reduce the case depth and hardness, and as a result, a gear might be fully cased only on burred corners, or in other instances might be properly nitrided with the exception of streaks across the tooth face corresponding to marks made by the cutting tool,

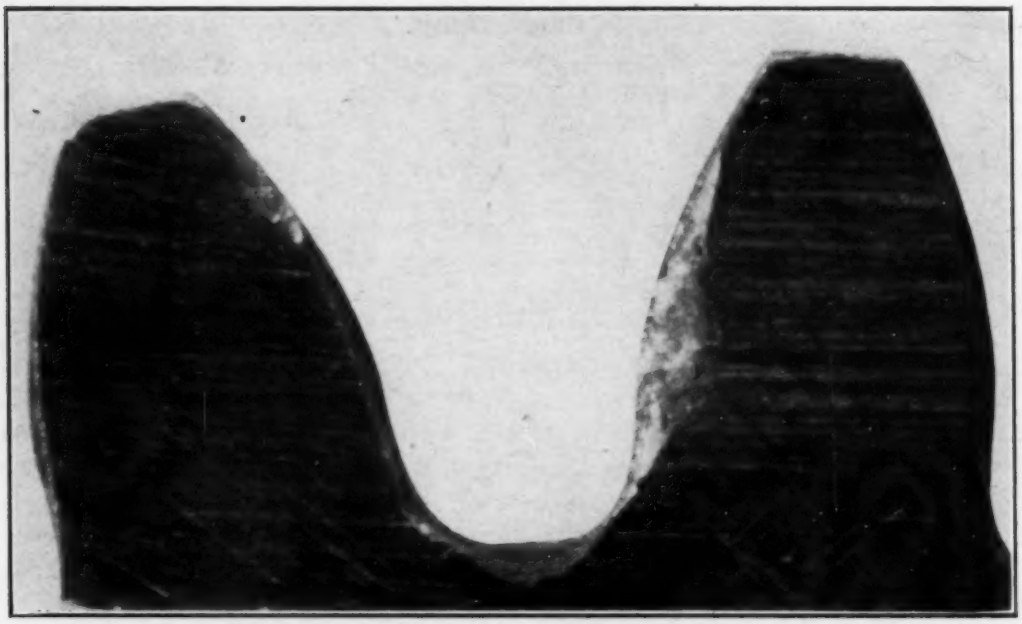

Fig. A—Semi-Finished and Nitrided Gear Showing Chipping of Sharp Corners. × 10.

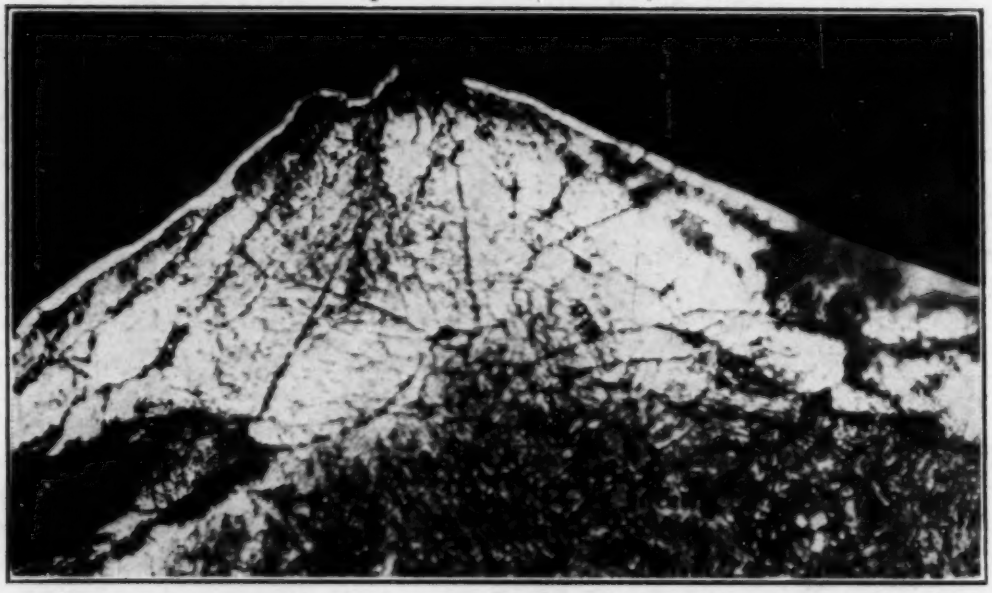

Fig. B—Photomicrograph Taken at the Edge of a Chipped Gear Tooth to Show Build-Up of White Nitride as Well as Chipping and Cracking Confined to the White Layer. Nital Etch. × 500.

which may have been dulled. Bonderized surfaces nitrided completely under all conditions of high dissociation. It is not believed that the increase in surface area resulting from the rougher finishes was responsible for the ability of such a surface to nitride better at very high dissociation since, in one case, adjacent ground faces on the same part had the same finish, as checked under binoculars and with a profilometer, but one face nitrided completely and the other not at all. Tin smear was never detected as a source of such variations.

It would seem reasonable to assume that the presence of even slight cold working of surfaces to be nitrided has an effect on the relationship between dissociation and the establishment of the white layer for dissociations in the neighborhood of 65 per cent or higher. Further information in this regard might be of value in establishing further practical limitations for the maximum permissible dissociation.

**Written Discussion:** By E. G. Mahin, professor of metallurgy and head, Department of Metallurgy, University of Notre Dame, Notre Dame, Ind.

The investigation reported in this paper has been carefully performed and reported as, from my earlier association with Dr. Floe's work, I should expect to be the case. I should like to raise only one question and this is concerning the chemical and physical mechanism of nitriding action. In this and in most other discussions it seems to be assumed, if not actually stated, that dissociation of ammonia taking place upon the steel surface permits the solution of a certain amount of atomic nitrogen in alpha iron, even though the major portion of the nitrogen resulting from dissociation immediately becomes molecular and inert. It has always seemed to me as a more likely explanation that molecular ammonia first dissolves in the surface layer of the iron, there undergoing dissociation and leaving nitrogen in solid solution, hydrogen largely, although not entirely, returning to the surrounding space.

I know of no experimental evidence for or against either theory and I should like to ask Dr. Floe to enlighten us on this point.

**Written Discussion:** By E. F. Bittner and Harry Stern, Detroit Gear Division, Borg-Warner Corp., Detroit.

This paper was of particular interest because it substantiates work done in our plants in production furnaces. It was found that good results could be obtained by maintaining a low dissociation for the first few hours of the cycle and then permitting it to rise up to 60 or 65 per cent. This effected a saving of about 40 per cent in ammonia used, with no deleterious effect on depth of penetration, hardness, or microstructure. In fact, some improvement was observed.

By such a cycle we put on a case of 0.017 to 0.019 inch, with a Rockwell 15N of 91 to 93, in 28 hours at 975 degrees Fahr. (525 degrees Cent.). Circulation of gases in the furnace is by fan so that high rate of ammonia input is not needed to prevent stagnant pockets.

Some experimental work was done to determine the amount of ammonia actually absorbed by the steel. Our results indicated that the nitrogen from about 2.5 per cent of the ammonia used was absorbed. This corresponds to about 12 per cent of the dissociated ammonia, which was a larger proportion than expected.

We have also had some experience with nitriding special analysis cast iron. In nitriding this material it is impossible to maintain low dissociation, possibly due to greater activity of the surface in catalyzing the reaction.

However, penetration or case depth is usually only about one-third that obtained on steel in the same load.

### Oral Discussion

R. A. RAGATZ:[2] In looking at one of Dr. Floe's illustrations I noted that

[2]Professor of chemical engineering, University of Wisconsin, Madison, Wis.

he was using per cent dissociation in the sense that it referred to per cent of nitrogen and hydrogen in the emergent gases. Now, that, of course, is not true percentage dissociation. I was just wondering for what particular reason the investigators in this field always used percentage dissociation in that particular sense.

GEORGE L. HANSEN:[3] What is the effect of an increase in temperature? You spoke of 975 degrees Fahr. (525 degrees Cent.) as the nitriding temperature. We ran some nitriding specimens at 1000 and at 1020 degrees Fahr. (540 and 550 degrees Cent.). What effect would the increase in temperature have on the skin effect?

M. H. MEDWEDEFF:[4] I would like to ask this question on dissociation. When you start a new piece of equipment, how can the degree of dissociation be controlled? When you get a maximum of 15 per cent, no matter what you do, how can it be raised, say, to 30 or 60 per cent?

ROLLAND R. LAPELLE:[5] I am wondering if any evidence was available as to whether or not the changes in dissociation rate above discussed had any particular effect on the hardness characteristics of the case as measured by the Vickers or any other means.

C. G. STUECKEN:[6] I would like to know a little more about the influence of the finish on the depth of formation of the white layer, whether sand-blasted finish, ground, or burnished finish.

JOHN L. DUNN:[7] We have been nitriding for several years. Until recently, we used a 48-hour nitriding cycle to nitride approximately 600 pounds of nitralloy. Through the purchase of new equipment, we have increased our nitriding heats to 2000 pounds and have lengthened our nitriding cycle to 72 hours. Since, we have experienced considerable difficulty in maintaining our ammonia dissociation, particularly in the last 36 hours of the heat. Does the size of the container in relation to the size of the load and the length of the nitriding cycle affect this trouble we are experiencing with our ammonia dissociation?

### Author's Reply

Mr. Hanink's remarks on the practical application of the results reported in this paper are very much appreciated. It is true that in the nitriding of some parts such as cylinder barrels, it is difficult to exceed 40 per cent dissociation of ammonia even by cutting the flow to a very low point. This condition only exists, however, for parts in which the surface area to be nitrided is small compared to the volume. The solution would be to construct a furnace in which a high rate of circulation of gas could be maintained with a very small flow rate of ammonia.

We are making a study of the effect of surface finish on nitriding. So far, however, nothing that we have been able to do to the surface has decreased the rate of nitriding. On the other hand, we have examined many highly polished

[3]Metallographist, Foote Brothers Gear & Machine Corp., Chicago.
[4]Metallurgical engineer, AC Spark Plug Division, General Motors Corp, Flint, Mich.
[5]Manager, Dempsey Industrial Furnace Corp., Springfield, Mass.
[6]N. A. Woodworth Co., Ferndale, Mich.
[7]Heat Treating Dept., The National Machinery Co., Tiffin, Ohio.

parts which have failed to nitride in commercial furnaces. The answer to this problem is not yet known. Light artificial oxidation of the surface, such as by bonderizing, is a good method of reducing any effect of surface finish. If tin plating is being used to prevent nitriding of certain areas, bonderizing has a further advantage of making it possible to readily detect any tin smears that may have been carried over by the grinding wheels onto areas to be nitrided.

Professor Mahin raises the question of whether or not actual nitriding is accomplished by molecular nitrogen which dissolves in the surface layer of iron and is then dissociated. There are two things wrong with this theory. In the first place, no nitriding results if iron is heated in molecular nitrogen gas. In the second place, nearly all experimental evidence now supports the theory that no gas dissolves in a metal in the molecular state. Even hydrogen must be broken down to the atomic state before it will dissolve.

The depths of case reported by Mr. Bittner and Mr. Stern for a 28-hour cycle are somewhat higher than those normally obtained. There are several factors that affect case depth which will be discussed in detail in a subsequent paper. The method of measurement is one important variable. Messrs. Bittner and Stern also state that their experimental work has shown that about 2.5 per cent of the ammonia used is absorbed. This figure is of the right order of magnitude. We have accurately determined the amount of nitrogen absorbed in nitriding and some figures will be given in the paper mentioned above.

Professor Ragatz questions the method of reporting the "percentage dissociation" of ammonia. The method, which is based upon the percentage of ammonia in the exhaust gases, is used purely because of convenience of measurement.

The effect of increasing the temperature of nitriding (question of Mr. Hansen) is to increase the case depth for a given time cycle, but to reduce the case hardness.

Mr. Medwedeff and Mr. Dunn raise the question of the factors affecting dissociation of ammonia. In a good nitriding installation ammonia should be dissociated only at the surfaces which are to be nitrided. Therefore, for a given flow rate of ammonia, the dissociation should increase with increasing load in the furnace. If the dissociation cannot be made to exceed 15 per cent, it means that the area of the work to be nitrided is too small compared to the lowest flow rate of ammonia that the means of adjustment will provide. Small loads should therefore not be placed in large furnaces.

The graphs shown in the paper answer the question raised by Mr. LaPelle on depth-hardness characteristics of cases produced at different dissociations of ammonia.

The question on effect of surface finish on nitriding asked by Mr. Stuecken has been answered above. Mr. Hanink's discussion also mentions this problem.

# THE ACTION OF CARBONATE CATALYSTS IN THE CARBURIZATION OF STEEL

By T. C. Fong and R. A. Ragatz

*Abstract*

*In Part I of the investigation, the evolution of carbon dioxide from plain charcoal and from charcoal catalyzed with sodium carbonate, barium carbonate or calcium carbonate was studied. Temperatures from 650 to 950 degrees Cent. (1200 to 1740 degrees Fahr.) were covered, and the times at temperature extended up to 7 hours. The curves relating time at temperature with per cent carbon dioxide evolved all level off after a short preliminary time at temperature, to constant values of per cent carbon dioxide evolved, the latter being dependent upon the temperature and the catalyst employed.*

*In Part II, the absorption of carbon dioxide by compounds catalyzed with sodium hydroxide or barium hydroxide was studied. It was observed that while the hydroxides were rapidly converted into carbonates at relatively low temperatures, the carbonates thus formed were decomposed at a rapid rate on heating to temperatures in the range commonly used for carburization.*

*In Parts III and IV two independent methods were employed whereby it was demonstrated that the catalytic activity induced by the addition of sodium carbonate or barium carbonate is sustained even after the per cent evolution of carbon dioxide had leveled off to a constant value.*

*It is proposed that in order for a carbonate catalyst to function effectively, two conditions must be fulfilled: (1) The carbonate must be capable of reacting directly with carbon (2) The carbonate must have a low dissociation pressure.*

## Introduction

THE widespread use of carbonate catalysts in carburizing compounds of the solid type is testimony to their effectiveness in accelerating the rate of carburization of steel. While it is universally

A paper presented before the Twenty-fifth Annual Convention of the Society, held in Chicago, October 18 to 22, 1943. Of the authors, T. C. Fong is instructor, and R. A. Ragatz is professor, Department of Chemical Engineering, University of Wisconsin, Madison, Wis. Manuscript received June 13, 1943.

recognized that certain carbonates are extremely effective as catalysts, there appears to be some divergence of opinion as to the mechanism of their action.

Without question, the most commonly offered explanation of the catalytic effect is the carbon dioxide evolution theory, which may briefly be outlined as follows. According to various writers (1 - 12)* the action of a catalyst such as barium carbonate is due to its dissociating into metallic oxide and carbon dioxide, according to the following reaction:

$$BaCO_3 \rightarrow BaO + CO_2$$

The carbon dioxide thus released reacts with the incandescent carbon to form carbon monoxide

$$C + CO_2 \rightarrow 2\,CO$$

The carbon monoxide formed by the foregoing reaction will react with the steel, resulting in the absorption of carbon by the austenite and the formation of carbon dioxide as a by-product.

$$2\,CO \rightarrow CO_2 + C \text{ (In Austenite)}$$

According to the foregoing explanation, the function of the carbonate catalyst is merely that of a source of carbon dioxide. While it is not always stated explicitly, it is implied that the catalyst undergoes decomposition in a progressive manner, and ultimately reaches a state of exhaustion after decomposition is completed. Following this line of reasoning, several writers have advocated that used carburizing compound be allowed to stand idle in contact with air for some time to permit "regeneration" of the compound by virtue of the absorption of carbon dioxide with consequent re-formation of the carbonate.

While some writers have held the simple carbon dioxide evolution theory as outlined above to be inadequate, or have accepted it with reservations (6), (9), (10), (13) (14), (15), (16), others have made a vigorous defense of the theory (4), (8), (11). In some of the experimental work of one of the present writers (15), (17) results were obtained which seemed to be incompatible with the carbon dioxide evolution theory as outlined above. The following facts were reported: (A) Certain carbonates which yield their carbon dioxide very readily, such as calcium carbonate or magnesium carbonate, for example, are entirely inert as catalysts. (B) Sodium

*The figures appearing in parentheses refer to the bibliography appended to this paper.

carbonate, bicarbonate, hydroxide, acetate, oxalate, cyanide, chromate and tungstate all exert catalytic effects of the same magnitude if they are added to the carburizing compound in such proportions that in each instance the same ratio exists between the sodium and the carbonaceous material. (C) Potassium carbonate, bicarbonate, hydroxide, acetate, oxalate, tetroxalate, cyanide, ferricyanide, ferrocynanide, chromate, dichromate and permanganate all exert catalytic effects of the same magnitude, provided they are added in such amounts that the same ratio between the potassium and the carbonaceous material exists in all instances. (D) Barium carbonate, oxide, hydroxide, acetate and nitrate all act in a similar manner, provided again that in the carburizing mixes, the same ratio between barium and the carbonaceous material exists in all instances. (E) Used carburizing compounds exhibited no capacity to regenerate on aging, even when exposed to an atmosphere of moist carbon dioxide for a protracted period of time.

Mahin (4), (8) has objected to some of the foregoing evidence presented against the carbon dioxide evolution theory, basing his argument upon some experiments wherein a study was made of the absorption of carbon dioxide occurring when barium oxide or calcium oxide were heated in the presence of carbon. He observed that on heating, the oxide was converted at least in part into carbonate at temperatures considerably below those used in carburization. He therefore argued that barium oxide, on heating, would be converted into the carbonate before the carburizing temperature is reached, and that on heating further, the carbonate thus formed would release its carbon dioxide gradually, and thus exert a catalytic effect by virtue of progressive and continuous evolution of carbon dioxide.

From the foregoing it is apparent that while some evidence has been presented against the carbon dioxide evolution theory, the theory still has its advocates. The purpose of the experimental work described in this paper was to carry out some studies which would throw further light on this controversial question.

The work performed may conveniently be divided into four parts: I. A detailed study was made of the decomposition of sodium carbonate, barium carbonate and calcium carbonate in the presence of charcoal, using various temperatures and various periods of time. II. A detailed study was made of the absorption of carbon dioxide when sodium hydroxide or barium hydroxide is heated

in the presence of charcoal. Various temperatures and time periods were employed. III. The rate of absorption of carbon by steel samples was studied, when using plain charcoal and when using compounds catalyzed with sodium carbonate or barium carbonate. The rate studies were correlated with the decomposition studies of Part I, to ascertain whether the rate of carburization was related to the rate of carbon dioxide evoluton from the compound. IV. Activity tests were carried out on compounds catalyzed with sodium or barium carbonate, and preheated prior to the introduction of the steel samples for such a time that evolution of carbon dioxide from the compound had ceased. The preheating time was chosen on the basis of the work performed in Part I, which indicated the preheating time needed to bring about cessation of carbon dioxide evolution.

## Experimental Procedures

Throughout the experimental work, hardwood charcoal was used as the carbonaceous base, since this material is widely used in commercial carburizing compounds. Material purchased from the Tennessee Eastman Corporation, and known to the trade as "Tec-Char No. 3" was used. Prior to use, it was reduced to powdered form. The powdered charcoal was analyzed for carbon dioxide, which was present in adsorbed form and also in the mineral matter of the charcoal. Due account was taken of the carbon dioxide content of the charcoal throughout the experimental work.

The carbonate catalysts used were all of reagent quality, and were powdered and dried prior to use.

The carburizing compounds were prepared shortly before they were to be used. Proper weights of the charcoal and of the catalyst were mixed in such a manner as to insure an even distribution of the catalyst throughout the compound.

The retorts used were made out of standard pipe fittings, using steel pipe nipples and black iron caps. The pipe nipples were pickled to remove galvanizing and the interior surfaces of the caps were machined to remove scale. Thus, a clean metal surface was obtained for the retort interior. Various sizes of fittings were used, appropriate to the needs of the various types of experiments performed. In assembling the retorts, one cap was screwed firmly onto a pipe nipple by means of a pipe wrench. After packing a retort with the desired charge, it was closed by screwing on a second cap by hand,

never to the extent of more than two or three complete turns. This procedure was followed with the deliberate intent of insuring that the retort interior would operate at atmospheric pressure, and yet not be subject to ready infiltration of air. It was felt that this procedure duplicated quite closely the conditions existing in commercial carburizing pots operating with solid compounds. The refractory luting used to close such containers does not provide a perfectly gas-tight seal. Equalization of pressure between the interior of the carburizing pot and the atmosphere is readily accomplished, and yet the luting prevents ready access of the air to the interior of the retort.

Temperature measurements were made by means of chromel-alumel couples, calibrated by a noble-metal couple having a Bureau of Standard certificate. Temperature control was obtained by means of a Leeds and Northrup Micromax controller-recorder.

In those instances where the charge was to be analyzed for its carbon dioxide content after heating for a certain period of time at a specific temperature, the charge after cooling was transferred to a flask and treated with boiling dilute hydrochloric acid. The carbon dioxide evolved was determined gravimetrically by absorption in Ascarite. Details of the procedures need not be given, as this method of analysis is standard and is described in many texts on analytical chemistry. It perhaps should be emphasized that at the expiration of the desired time at temperature, the retort containing the charge was removed from the furnace and air-cooled. Slow cooling would have permitted re-formation of carbonate, at least to some extent, and the analytical results would then have been of no significance. It was demonstrated by experiment that air cooling of the retorts produced results identical with those obtained with water quenching. This indicates that air cooling is sufficiently rapid to prevent re-formation of carbonate, and indicates that the analytical results indicate the true carbon dioxide content of the compound at the close of the heating period, prior to cooling.

## Part I

### Evolution of Carbon Dioxide from Carburizing Compounds

The purpose of this portion of the experimental work was to test the assumption involved in the carbon dioxide evolution theory

that the carbonate catalyst releases its carbon dioxide in a gradual and progressive fashion. Tests were carried out on pure charcoal, and on compounds prepared by mixing 90 per cent of charcoal with 10 per cent of catalyst. The catalysts used were sodium carbonate, barium carbonate and calcium carbonate.

The retorts, after charging, were placed into a cold electric furnace, and the assembly was brought to the desired heat treating temperature by employing the maximum safe heating current. Heat

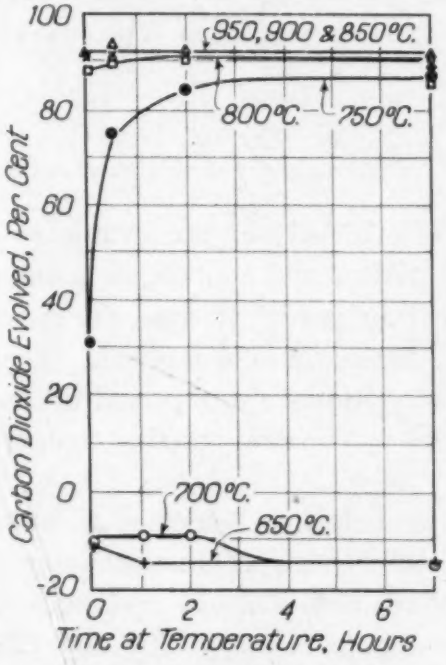


Fig. 1—Evolution of Carbon Dioxide from Plain Charcoal at Various Temperatures.

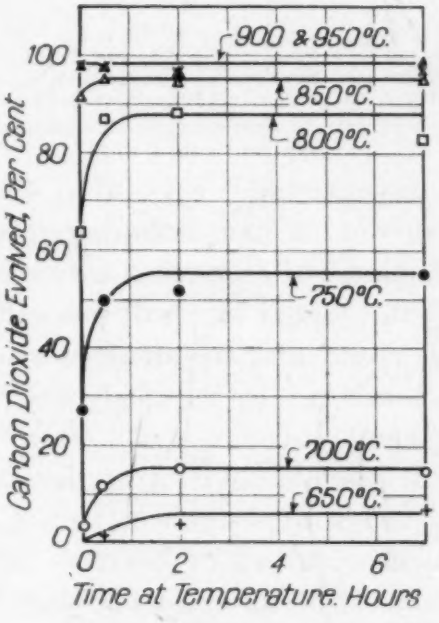


Fig. 2—Evolution of Carbon Dioxide from Mixtures of Charcoal and Sodium Carbonate at Various Temperatures.

treatments were carried out at 650, 700, 750, 800, 850, 900 and 950 degrees Cent. (1200, 1290, 1380, 1470, 1560, 1650 and 1740 degrees Fahr.). The heating times at temperature in most instances ranged from 0 to 7 hours, a time period of 0 indicating that the retort was merely brought up to the desired heat treating temperature, and then removed from the furnace. At the expiration of the desired time at temperature, the retorts were removed and air-cooled, after which the charge was analyzed for its carbon dioxide content.

The results obtained are summarized in Figs. 1 to 4. Each point indicated is the average of the results obtained with at least two retorts of the carburizing compound.

In interpreting the results, it will be necessary to keep in mind

that the carbon dioxide in the original charge is present both in the charcoal itself and also in the catalyst. The following table indicates the distribution of carbon dioxide between the charcoal and the catalyst:

**Table I**
**Distribution of Carbon Dioxide in the Charge Previous to Heat Treatment**

| Carburizing Compound | Percentage of Total Carbon Dioxide Present | |
|---|---|---|
| | In the charcoal Per Cent | In the catalyst Per Cent |
| 1. Plain charcoal | 100.0 | — |
| 2. 90 per cent charcoal + 10 per cent $Na_2CO_3$ | 25.6 | 74.4 |
| 3. 90 per cent charcoal + 10 per cent $BaCO_3$ | 39.8 | 60.2 |
| 4. 90 per cent charcoal + 10 per cent $CaCO_3$ | 25.1 | 74.9 |

In examining Figs. 1 to 4, it is evident that the evolution of carbon dioxide does not proceed in a gradual and continuous manner. As a matter of fact, after a relatively short period of time, the curves level off to fixed values of percentage carbon dioxide evolved. These fixed values that are assumed after a relatively short period of time are determined by the catalyst used and by the heat treating temperature employed.

It may be noted that the low temperature behavior of mixes catalyzed with sodium carbonate is different from the behavior of plain charcoal or of charcoal catalyzed with barium carbonate or calcium carbonate. At 650 and 700 degrees Cent. (1200 and 1290 degrees Fahr.) mixes catalyzed with sodium carbonate show a well-defined evolution of carbon dioxide, whereas the other compounds exhibit an absorption of carbon dioxide.

Another point worthy of mention, which will be brought up later in the discussion of a proposed mechanism of catalytic activity, is that in no instance does the percentage of carbon dioxide evolved reach 100 per cent. There always appears to be a certain quantity of residual carbon dioxide in the system, even at the highest temperatures employed.

By interpreting the curves of Figs. 2 to 4 in relation to Table I, certain deductions may be made with respect to the decomposition of the carbonate catalyst. If any curve for a given catalyst as given in Figs. 2 to 4 rises above the value given in Table I for the percentage of the total carbon dioxide present in the charge which exists in the charcoal, it may be stated with positive assurance that decomposition

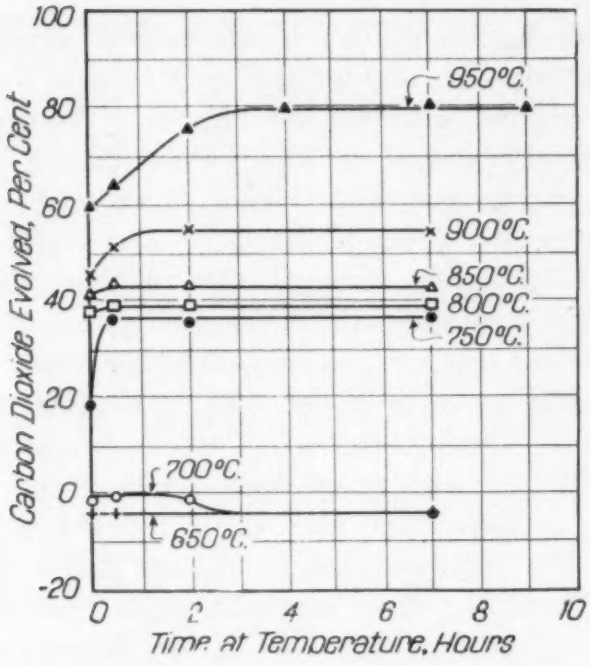


Fig. 3—Evolution of Carbon Dioxide from Mixtures of Charcoal and Barium Carbonate at Various Temperatures.

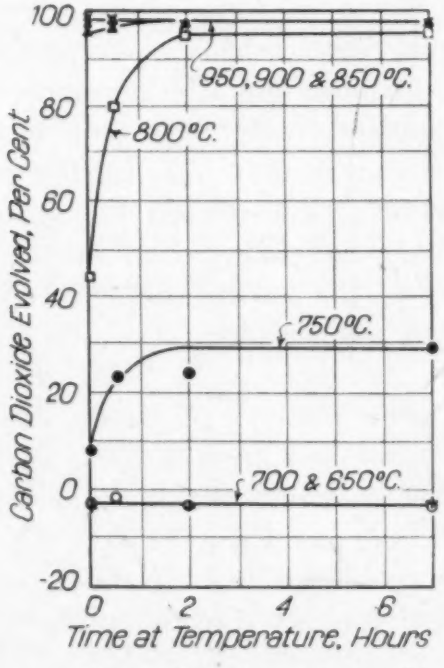


Fig. 4—Evolution of Carbon Dioxide from Mixtures of Charcoal and Calcium Carbonate at Various Temperatures.

of the catalyst must have occurred. For example, in the case of the sodium carbonate catalyst, Table I indicates that 25.6 per cent of

the total carbon dioxide present in the original charge was in the charcoal. Referring now to Fig. 2, it may be seen that at temperatures of 750 degrees Cent. (1380 degrees Fahr.) and over, the curves level off at values of per cent carbon dioxide evolved which are in excess of 25.6 per cent. Hence, it may be concluded with positive assurance that at temperatures of 750 degrees Cent. (1380 degrees Fahr.) and over, decomposition of the sodium carbonate occurs. A similar analysis of the curves in Figs. 3 and 4 in relation to Table I indicates that with barium carbonate catalyst, decomposition unquestionably occurs at 850 degrees Cent. (1560 degrees Fahr.) and over, while with calcium carbonate, decomposition unquestionably occurs at 750 degrees Cent. (1380 degrees Fahr.) and over.

The next question that may be considered pertains to the mechanism of the decomposition of the carbonate catalyst. Does decomposition occur by direct dissociation into metallic oxide and carbon dioxide, or is there direct interaction between the carbonate and the carbon? Conclusions pertaining to this question may be drawn from a consideration of plots similar to those shown in Fig. 5. In Fig. 5, the three curves show, respectively, the decomposition pressure of sodium carbonate, the partial pressures of $CO_2$ for the C: CO: $CO_2$ equilibrium at 1 atmosphere pressure when the gaseous phase is composed only of carbon monoxide and carbon dioxide and the partial pressure of $CO_2$ for the C: CO: $CO_2$ equilibrium at 1 atmosphere pressure when the gases are diluted with atmospheric nitrogen. The intersection of the curve for the decomposition pressure of the sodium carbonate with the other curves determines the lowest temperatures at which direct dissociation of the sodium carbonate can occur. Fig. 5 indicates that when sodium carbonate is heated in the presence of carbon, direct dissociation cannot possibly occur below 863 degrees Cent. (1585 degrees Fahr.). Since Fig. 2 indicates a definite decomposition of sodium carbonate at 750, 800 and 850 degrees Cent. (1380, 1470 and 1560 degrees Fahr.), it must be concluded that at these temperatures, sodium carbonate and carbon interact directly, probably according to the following reaction.

$$Na_2CO_3 + 2C \rightarrow 2\,Na + 3\,CO$$

In the case of the barium carbonate catalyst, a plot similar to Fig. 5 indicates that direct dissociation cannot occur in the presence of carbon at temperatures below 960 degrees Cent. (1760 degrees

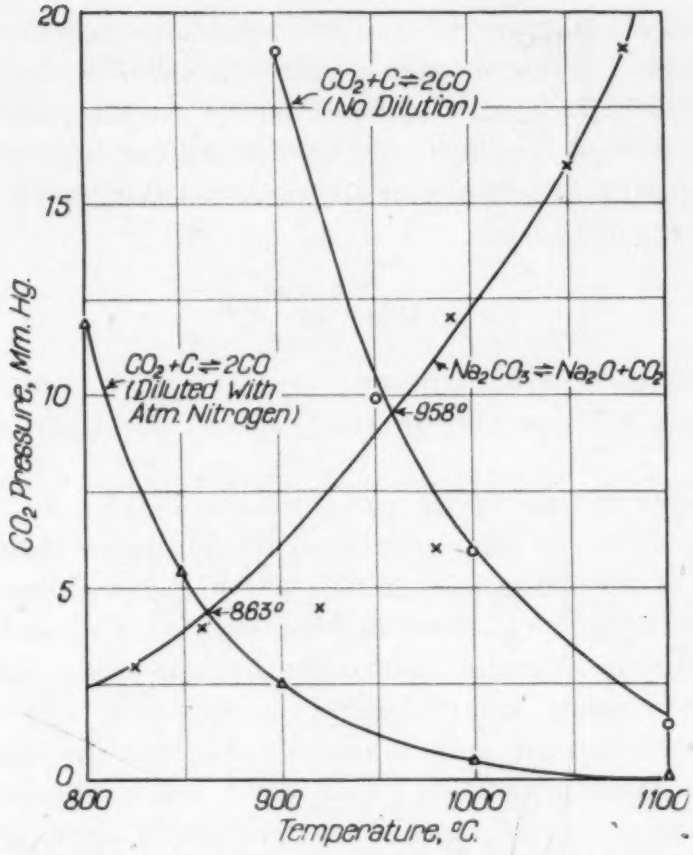


Fig. 5—Minimum Temperature of Direct Decomposition of $Na_2CO_3$ in the Presence of Carbon at One Atmosphere Pressure.

Fahr.). Analysis of the curves shown in Fig. 3 indicated that decomposition unquestionably did occur at temperatures of 850, 900, and 950 degrees Cent. (1560, 1650, and 1740 degrees Fahr.), hence, it must be concluded that direct interaction between carbon and barium carbonate is possible at these temperatures. In the case of barium carbonate, no investigators have shown the possibility of reducing it to the metallic state, hence the probable reaction is as follows:

$$BaCO_3 + C \rightarrow BaO + 2\,CO$$

In the case of calcium carbonate, a set of curves similar to those of Fig. 5 indicate that calcium carbonate can dissociate directly in the presence of carbon, at temperatures of 724 degrees Cent. (1335 degrees Fahr.) and over. It has already been pointed out that the curves of Fig. 4 indicate that a definite decomposition of calcium carbonate occurs at temperatures of 750 degrees Cent. (1380 degrees Fahr.) and over. In the present instance, however, the de-

composition can occur by direct dissociation into metallic oxide and carbon dioxide. Since, at temperatures below 750 degrees Cent. (1380 degrees Fahr.), no decomposition of calcium carbonate can be obtained, it must be concluded that calcium carbonate and carbon do not interact directly and that the observed decomposition is due solely to direct dissociation.

## Part II

### The Rate of Carbon Dioxide Absorption by Sodium and Barium Hydroxide in the Presence of Carbon

In a paper by one of the present writers (15), it was shown that sodium hydroxide and sodium carbonate exert identical catalytic effects if the carburizing mixes are so proportioned that the same ratio between the charcoal and the sodium exists in both compounds. Likewise, barium hydroxide, barium oxide and barium carbonate exert similar catalytic effects if the carburizing mixes are so proportioned that the same ratio exists between the charcoal and the barium in both instances. From this it was concluded that the carbonate content of the catalyst is of no significance, and hence, that the carbon dioxide evolution theory of energizer action was not valid. Mahin (4), (8) has objected to this line of reasoning on the grounds that if a hydroxide or an oxide is heated in a retort containing carbon and an atmosphere of carbon dioxide and carbon monoxide, the hydroxide or oxide will be converted into carbonate on heating up the system, and that when the carburizing temperature is reached, the same quota of carbon dioxide will be released by the catalyst, as if it originally had been present in the carbonate form rather than the hydroxide or oxide form. Since Mahin presented a limited amount of data, showing that barium oxide was converted in part to barium carbonate when heated with carbon, it was felt that a more detailed study would be desirable. Accordingly, experiments as detailed in this section were carried out, wherein the degree of absorption of carbon dioxide was studied for mixes containing sodium hydroxide and barium hydroxide as catalysts.

The experimental procedures were similar to those for Part I. The sodium and barium hydroxides were analyzed, so the mixes could be proportioned in such a manner that the ratio between the weight of charcoal and the weight of the metallic portion of the

catalyst was the same as in Part I, where mixes composed of 90 per cent charcoal and 10 per cent carbonate catalyst were used.

The experimental results are summarized in Figs. 6 and 7, wherein per cent carbon dioxide absorbed is plotted against time at heat treating temperature, at various fixed temperature values.

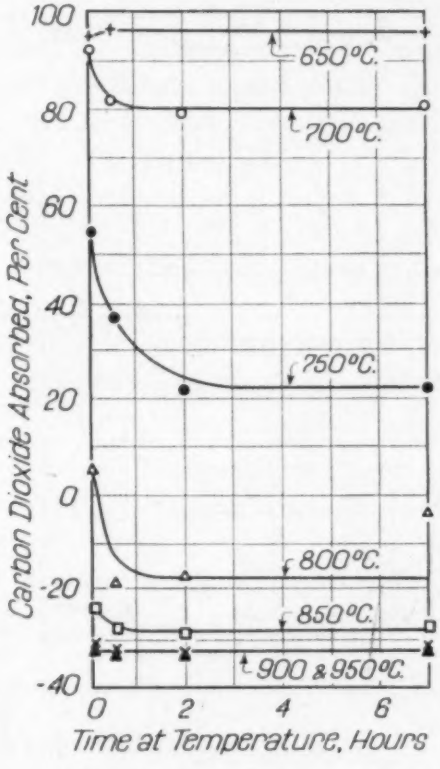


Fig. 6—Absorption of Carbon Dioxide by Mixtures of Sodium Hydroxide and Charcoal at Various Temperatures.

Values for per cent carbon dioxide absorbed were computed as follows:

$$\text{Per cent Absorption} = \frac{\left[\begin{array}{c}\text{Weight of } CO_2 \text{ found} \\ \text{after heat treatment}\end{array}\right] - \left[\begin{array}{c}\text{Weight of } CO_2 \text{ present} \\ \text{before heat treatment}\end{array}\right]}{\left[\begin{array}{c}\text{Weight of } CO_2 \text{ needed for complete conversion} \\ \text{of the hydroxide to the carbonate}\end{array}\right]} \times 100$$

Thus, a value of zero for per cent absorption would signify that the heat treatment produced no change in the carbon dioxide content. A positive value would signify a net absorption of carbon dioxide, whereas a negative value would indicate a net loss of carbon dioxide. For the compounds catalyzed with sodium carbonate, the largest possible negative value is —36.7 per cent, which would correspond to

complete removal of carbon dioxide from the system. In the case of the barium hydroxide catalyst, the value corresponding to complete removal of carbon dioxide is —68.3 per cent.

Inspection of Figs. 6 and 7 shows that very rapid conversion into the carbonate is obtained at low temperatures, but that subse-

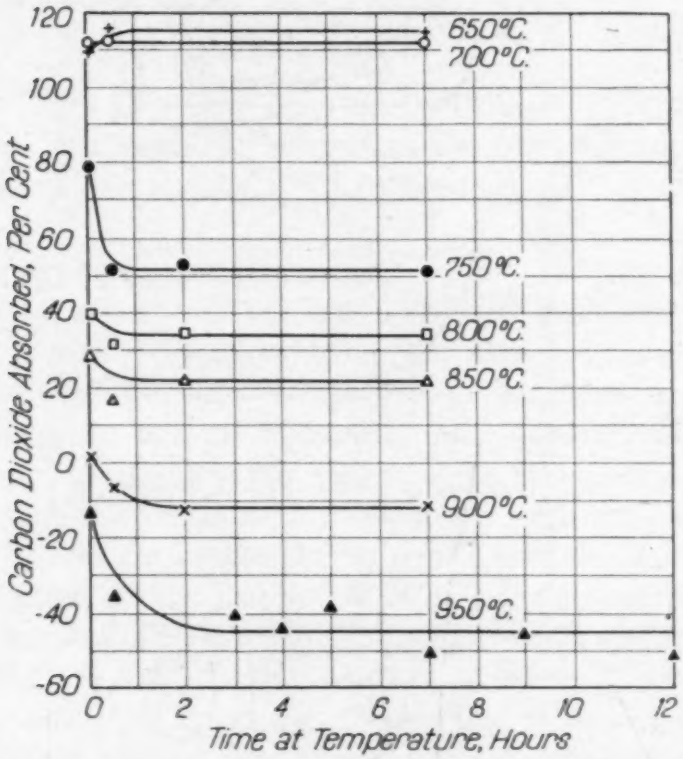


**Fig. 7—Absorption of Carbon Dioxide by Mixtures of Barium Hydroxide and Charcoal at Various Temperatures.**

quent decomposition is very rapid if heating is continued to the higher temperatures normally used in carburization. For example, referring to Fig. 6 for compounds catalyzed by the addition of sodium hydroxide, it is evident that on heating to 650 degrees Cent. (1200 degrees Fahr.), a value of 95 per cent absorption is secured. However, if heating is continued, and the temperature is brought to 900 or 950 degrees Cent. (1650 or 1740 degrees Fahr.), decomposition is very rapid. The curves at these temperatures are at a value of approximately —33 per cent absorption for zero hours at temperature, which is a close approach to the limit of —36.7 per cent which would be obtained if all of the carbon dioxide were driven from the system.

Similar remarks may be made with respect to the barium hydroxide catalyst.

It may therefore be concluded that Mahin is correct in his contention that the hydroxides of sodium or barium are converted into the corresponding carbonates when heated in the presence of carbon. However, his assumption that the carbonate thus formed releases its carbon dioxide in a gradual and progressive fashion if the system is heated to higher temperatures is not borne out by these experimental results.

## Part III

### The Rate of Carburization of Steel by Compounds Using Sodium Carbonate or Barium Carbonate as a Catalyst

According to the simple carbon dioxide evolution theory, a catalyst should become ineffective after it has ceased evolving carbon

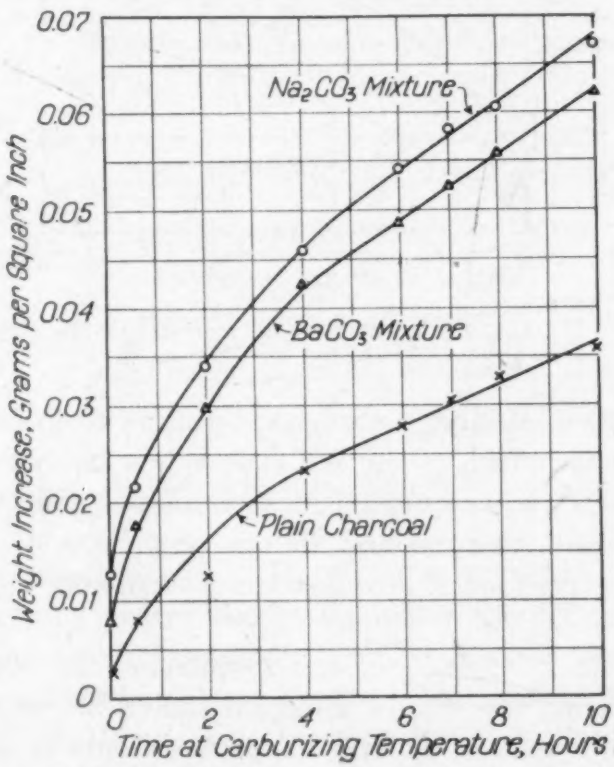


Fig. 8—Carburization of Steel at 950 Degrees Cent. (1740 Degrees Fahr.)

dioxide. In this section, experiments are described wherein the rate of carbon absorption by steel was studied as a function of time, at several heat treating temperatures. Such studies were made with

plain charcoal as the carburizing agent, and with mixes composed of charcoal with either sodium carbonate or barium carbonate as catalyst. It was felt that by correlating the results of these tests with the previous work on the rate of decomposition of the carbonates, some conclusions might be drawn as to whether or not a catalyst lost its accelerating effect upon carburization after it ceased to yield carbon dioxide.

The degree of carburization accomplished by a given heat treatment was evaluated by determining the weight increase of cylinders

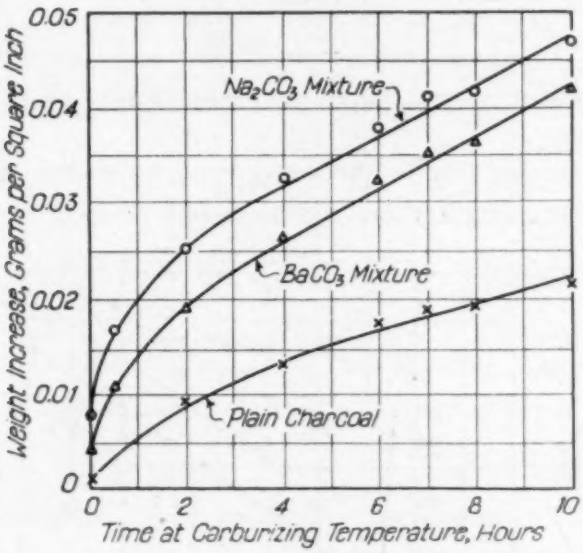


**Fig. 9—Carburization of Steel at 900 Degrees Cent. (1650 Degrees Fahr.)**

of S.A.E. 1020 steel, and reducing the results to grams of carbon absorbed per square inch of surface area. When catalysts were added to the charcoal, they were added in such amount that the mix contained 90 per cent charcoal and 10 per cent catalyst. The details regarding the experimental methods are substantially as described in a previous paper (17).

The results of these tests are summarized in Figs. 8 to 11.

In interpreting the results, attention should be paid to the relative slopes of the curves, making comparisons only at identical conditions of temperature and time. The slope of a curve at a given point indicates the rate of carbon absorption as grams per square inch per hour, and this evidently is a direct measure of the rate of carburization. Hence, by noting the relative slopes for the three carburizing mixes at identical conditions of temperature and times,

conclusions may be drawn regarding the relative activity of the three carburizing mixes. Should a catalyst become exhausted, the slope of the curve for the compound containing the catalyst should become the same as the slope of the curve for pure charcoal.

Fig. 8 shows the results obtained at 950 degrees Cent. (1740 degrees Fahr.). It is to be noted that for time periods ranging from 0 to 10 hours at temperature, the curve for the compound containing

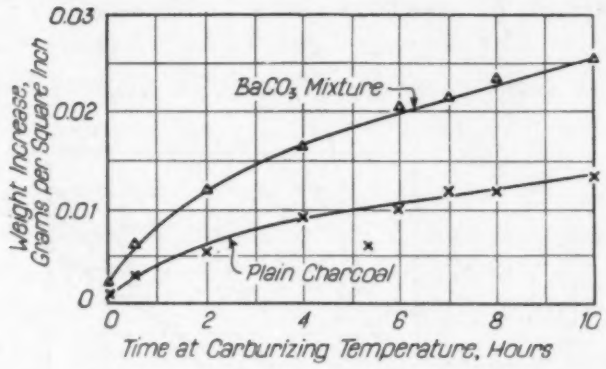


**Fig. 10—Carburization of Steel at 850 Degrees Cent. (1560 Degrees Fahr.)**

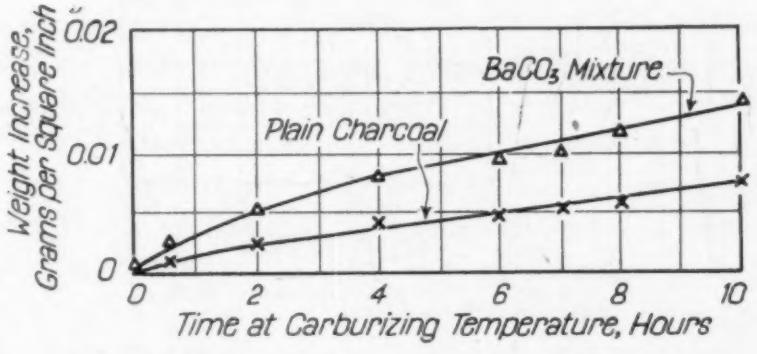


**Fig. 11—Carburization of Steel at 800 Degrees Cent. (1470 Degrees Fahr.)**

sodium carbonate and the curve for the compound containing barium carbonate exhibit greater slopes than does the curve for plain charcoal, the comparisons being made, of course, at identical values of time at the carburizing temperature. This indicates very definitely that even after 10 hours at temperature, the catalysts are not exhausted, and are still exerting an accelerating effect on the rate of carburization. From the work on the decomposition of carbonates described previously, it is known that at 950 degrees Cent. (1740 degrees Fahr.), there is no evolution of carbon dioxide from a mix catalyzed with sodium carbonate, after 950 degrees Cent. (1740 de-

grees Fahr.) is reached on heating. (See Fig. 2). Furthermore, with respect to barium, it was shown that at 950 degrees Cent. (1740 degrees Fahr.), no evolution of carbon dioxide occurs after the charge has been at temperature three hours. (See Fig. 3). The results, accordingly, seem to indicate very definitely that progressive decomposition of the carbonate catalyst is not essential to its accelerating the rate of carburization.

The results at 900 degrees Cent. (1650 degrees Fahr.) parallel those obtained at 950 degrees Cent. (1740 degrees Fahr.), and require no further comment. At 850 and 800 degrees Cent. (1560 and

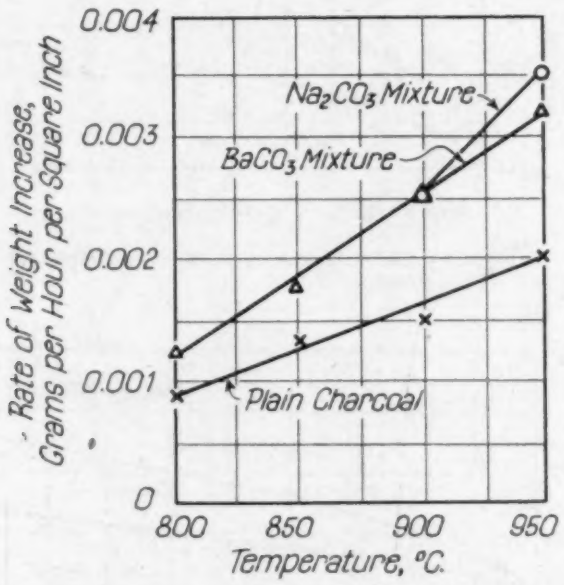


Fig. 12—Rate of Carburization of Steel at Various Temperatures.

1470 degrees Fahr.), a heavy adherent deposit of graphite was produced on the specimens treated with the carburizing compound containing sodium carbonate, hence the weight increases obtained in these cases were not reliable, and are not included. The results obtained with the barium carbonate catalyst, however, are similar to those obtained at 950 and 900 degrees Cent. (1740 and 1650 degrees Fahr.), and the same general conclusions may be drawn.

In examining Figs. 8 to 11, it will be noted that the curves beyond approximately the first four hours become substantially straight lines, indicating a nearly constant rate of carburization. The slopes of the curves in the range where they are substantially straight lines were determined, and are plotted against temperature in Fig.

12. It will be noted that the rates of carburization when using compounds catalyzed with sodium carbonate or barium carbonate are higher at all of the temperatures covered than is the rate of carburization when using plain charcoal. It is to be emphasized that the rate values plotted in Fig. 12 were those established after four hours of heating, when the carbonate catalysts were not undergoing progressive decomposition.

## Part IV

### Test of Catalytic Activity After Evolution of Carbon Dioxide Has Stopped

From the experimental work carried out on the decomposition of carbonates in the presence of carbon, it was possible to ascertain the time required for the evolution of carbon dioxide to cease at various temperatures and with various carbonates. Examination of Figs. 1 to 4 will show that after six hours at temperature, for temperatures of 800, 850, 900 and 950 degrees Cent. (1470, 1560, 1650 and 1740 degrees Fahr.), evolution of carbon dioxide from the system has long since stopped, regardless of whether plain charcoal is used or charcoal catalyzed either with sodium carbonate, barium carbonate or calcium carbonate.

It was believed that significant conclusions could be drawn if tests were run wherein the steel specimens were not introduced into the retorts until the carburizing compound had been at temperature for a period of six hours. If it is correct that catalytic activity ceases when carbon dioxide evolution ceases, the plain charcoal should, under these conditions, carburize the steel specimens to exactly the same degree as the compounds that originally contained sodium carbonate or the compounds that originally contained barium carbonate. On the other hand, if it should develop from the experimental work that the specimens treated with the mixes which originally contained either sodium carbonate or barium carbonate were carburized to a greater degree than those carburized with plain charcoal, the conclusion would inevitably follow that progressive decomposition of the catalyst with consequent evolution of carbon dioxide is not necessary to an effective catalytic effect.

The carburizing compounds used in this part of the experimental program were either plain charcoal or mixes containing 90 per cent charcoal and 10 per cent carbonate catalyst.

The retorts, made out of pipe fittings of suitable size, had a hole drilled in the top cap, of sufficient diameter to permit the introduction of the steel pin to be carburized. The retort was charged in the usual way, but instead of introducing the steel pin to be carburized, the hole was closed by means of a steel plug of the same diameter as the pin to be introduced later. This plug was luted in place by means of alundum cement. The carburizing retort was then heated to the desired temperature, and held at temperature for

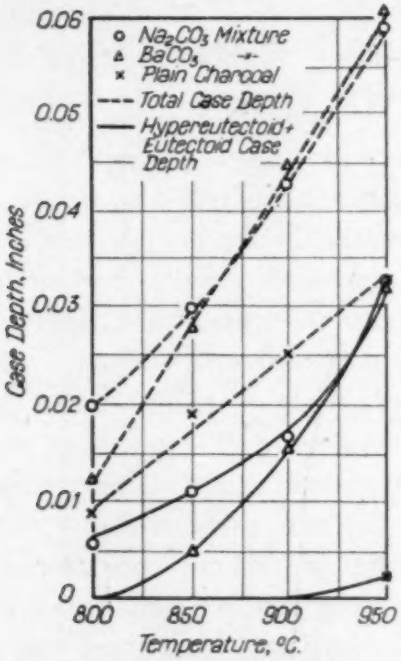


**Fig. 13—Catalyst Activity Tests in the Carburization of Steel.**

six hours. From the work performed in Part I, it was known that this time was more than sufficient to bring about cessation of carbon dioxide evolution from the compound. At the close of the 6-hour period at temperature, the plug was removed, and the pin to be carburized was quickly inserted through the hole. The upper end of the pin had a flange that rested against the outside surface of the top cap of the retort. The lower surface of this flange carried alundum cement which established a cemented seal after insertion of the test pin. The heat treatment was continued for six more hours, after which the retort assembly was removed from the furnace and air-cooled. Subsequently, the test pin was removed from the retort, and after sectioning, polishing and etching, the depth of case was determined by measurement with a filar micrometer.

From the foregoing, it is apparent that a cold specimen was introduced into the hot retort. It could therefore be argued that this procedure might cause the interior temperature of the retort to drop to such a degree that significant re-formation of the carbonate catalyst might result. To forestall this objection, tests were carried out wherein a pin was preheated to the carburizing temperature before it was introduced into the hot retort. Practically identical results were obtained, regardless of whether the pin was preheated or not.

The results of the experiments pertaining to this section are summarized in Fig. 13. Every point on the graph represents the average of two or more specimens. The curves clearly indicate that the compounds to which sodium carbonate or barium carbonate had been added still exerted a marked catalytic effect, even though the compounds had been preheated 6 hours prior to the introduction of the steel specimens. This leads to the conclusion that progressive decomposition of the carbonate catalyst with a resulting evolution of carbon dioxide is not necessary to the maintenance of a catalytic effect.

## General Conclusions

1. The curves showing per cent carbon dioxide evolved at various temperatures as a function of time all level off to constant values of per cent carbon dioxide evolved after a relatively short period of time at temperature. This is true whether the compound is plain charcoal, or charcoal to which sodium carbonate, barium carbonate or calcium carbonate has been added. In general, the higher the temperature, the greater the per cent carbon dioxide evolved, though at the higher temperatures the curves are practically coincident. There is no evidence to indicate that in the carburization of steel, the carbonate catalysts decompose in a progressive and continuous fashion throughout the carburizing period. Everything indicates that at temperatures normally used in carburization, the decomposition of the carbonate catalyst ceases shortly after the carburizing temperature is reached.

2. The results indicate that at even the highest temperatures employed, there is always some residual carbon dioxide present in the compound that is not driven out even on protracted heating. This leads to the hypothesis that even though there may be no net decomposition of carbonate occurring in the compound, a state of

dynamic equilibrium is established which results in the re-formation of carbonate as fast as it is decomposed.

3. The experimental results clearly indicate that direct interaction between carbon and sodium carbonate occurs at temperatures below the minimum temperature at which sodium carbonate can dissociate directly in the presence of carbon. A similar observation was made for barium carbonate heated in the presence of carbon. In the case of calcium carbonate, however, no reaction with carbon seems to occur.

4. Mahin's observation that oxides and hydroxides added to a carburizng compound will revert to the carbonate on heating was verified. However, his assertion that the carbonate thus formed releases its carbon dioxide slowly when heated to higher temperatures was not verified. In fact, the data in the present paper show an extremely rapid release of carbon dioxide on heating to higher temperatures.

5. It has been demonstrated that compounds catalyzed with either sodium carbonate or barium carbonate exhibit a sustained superiority over plain charcoal, even after the decomposition of the carbonate has leveled off to a fixed value.

## Proposed Mechanism of the Catalytic Effect Produced by Certain Carbonates

In the absence of a carbonate catalyst, the transfer of carbon from the carbonaceous substance to the steel is accomplished by the concurrent diffusion of carbon monoxide from the carbon : gas interface to the gas : steel interface and of carbon dioxide in the opposite direction. There are but two reactions involved in the process, the one at the gas : steel interface being

$$2\,CO \rightarrow CO_2 + C \text{ (In Austenite)} \quad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

and the one at the gas : carbon interface being

$$CO_2 + C \rightarrow 2\,CO \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

It is proposed that the addition of the sodium carbonate catalyst to the carburizing agent accelerates the rate of carburization because of producing the following effects. As the system is being heated up to the carburizing temperature and while it is being held at the carburizing temperature, the sodium carbonate reacts with the car-

bon, even though the temperature may be well below the minimum temperature at which direct dissociation into sodium oxide and carbon dioxide can occur.

$$Na_2CO_3 + 2\,C \rightarrow 2\,Na + 3\,CO \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

Both of the products of the reaction speed up the rate of carburization because of the following effects. The carbon monoxide generated creates a higher concentration of carbon monoxide in the gaseous phase at the carbon : gas interface than exists in the absence of such a reaction. This higher carbon monoxide concentration speeds up the rate of diffusion of carbon monoxide to the gas : steel interface. The sodium vapor generated by the reaction also exerts an important effect, because of its marked affinity for carbon dioxide, the by-product of the carburizing reaction.

$$CO_2 + 2\,Na \rightarrow Na_2O + CO \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

The sodium oxide thus formed will also tend to absorb carbon dioxide, because of the low dissociation pressure of sodium carbonate in relation to the equilibrium pressure of carbon dioxide at the gas : steel interface.

$$Na_2O + CO_2 \rightarrow Na_2CO_3 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

The sodium carbonate thus formed is free to react with the carbon, and the cycle will be repeated indefinitely.

As the system is being heated up to temperature, there will be a considerable evolution of gas from the retort, because of simple thermal expansion, and also because of reaction 3 coming into play. In addition, adsorbed gases present in the carbonaceous substance will be given off. Shortly after the system has come to temperature, however, the evolution of gas from the retort will cease. A condition of dynamic balance will be achieved, with reactions 1 to 5 occurring concurrently and continuously. This will result in there always being a certain residual and constant quality of carbon dioxide in the carburizing compound.

One other factor comes into play which tends to speed up the rate of carburization. In a previous paper by one of the present writers (17), it was demonstrated that when sodium carbonate and barium carbonate were used as catalysts, a finely divided precipitate, presumably graphite, was invariably found on the surface of the steel. This precipitate in all probability arises because reaction No. 3 produces a carbon monoxide concentration in the main mass

of the gaseous phase that is considerably higher than the equilibrium value for Reaction 2. When this fine precipitate forms on the steel surface, the distance over which gaseous diffusion must occur is reduced, tending to speed up carburization.

The situation is similar with respect to the barium carbonate catalyst, except that no investigators have reported that metallic barium could be formed by a reaction analogous to No. 3. The initial reaction of the cycle is as follows:

$$BaCO_3 + C \rightarrow BaO + 2\,CO \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

The carbon monoxide thus formed speeds up carburization for the same reasons as advanced when sodium carbonate was under discussion. The acceleration in the removal of the carbon dioxide resulting from carburization is accomplished largely because of the low dissociation pressure of the barium carbonate, which promotes the reaction between the barium oxide and the carbon dioxide.

$$BaO + CO_2 \rightarrow BaCO_3 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

The foregoing cycle can be maintained indefinitely. Again, after the carburizing temperature has been maintained for a short period of time, a condition of dynamic balance will be established, with reactions 1, 2, 6 and 7 occurring simultaneously and continuously. The formation of a finely divided precipitate of graphite on the surface of the steel is also a factor tending to speed up carburization, as was pointed out in the discussion pertaining to sodium carbonate.

In general, sodium carbonate and barium carbonate are effective catalysts because: (A) They are able to react with carbon at temperatures below the minimum temperature for direct dissociation into metallic oxide and carbon dioxide (B) The products of the reaction accelerate the rate of carburization by increasing carbon monoxide concentration and also by speeding up removal of carbon dioxide.

In Table II are listed some data which show the relation between dissociation pressure and ability to act as effective catalysts in the carburization of steel. In Group I, the ineffective materials are listed, and it will be noted that the dissociation pressures are very high. In these instances, the substances will undergo rapid decomposition, not by reacting with carbon, but by direct dissociation. The products of this direct dissociation are carbon dioxide and metallic oxide. The formation of these products will not tend to speed up carburization. The carbon dioxide must first be converted into

**Table II**
**Carbon Dioxide Pressures for Various Equilibria at 900 Degrees Cent. (1652 Degrees Fahr.)**

| No. | Group | Equilibrium | $p_{CO_2}$ Pressure mm Hg | Δp mm Hg | Remarks | Literature Reference |
|---|---|---|---|---|---|---|
| 1 | I | $MgCO_3 \rightleftarrows MgO+CO_2$ | No data | — | p=10 atm at 498° C. (928° F.) | 18 |
| 2 | I | $CaCO_3 \rightleftarrows CaO+CO_2$ | 956 | −932 | | 18 |
| 3 | II | $Na_2CO_3 \rightleftarrows Na_2O+CO_2$ | 6.38 | 17.3 | Data uncertain See Fig. 5 | 19 |
| 4 | II | $K_2CO_3 \rightleftarrows K_2O+CO_2$ | 3.50 | 20.2 | | 19 |
| 5 | II | $SrCO_3 \rightleftarrows SrO+CO_2$ | 5.91 | 17.8 | | 18 |
| 6 | II | $2BaCO_3 \rightleftarrows BaO.BaCO_3+CO_2$ | 0.53 | 23.2 | | 18 |
| 7 | II | $BaO.BaCO_3 \rightleftarrows 2BaO+CO_2$ | 0.20 | 23.5 | | 18 |
| 8 | III | $2CO \rightleftarrows CO_2+C$ (Graphite) | 19.1 | 4.6 | | 20 |
| 9 | III | $2CO \rightleftarrows CO_2+C$ (In Sat'd. Austenite) | 29.6<br>40.3<br>12.9<br>12.0<br>23.7 Av. | | | 21<br>22<br>23<br>24 |

For reactions 8 and 9: Total pressure = 1 atm.
: Gaseous atmosphere of CO and $CO_2$ only.
Δp = (p for reaction 9) — (p for reaction in question)

the monoxide before it becomes effective. The metallic oxide will have no capacity to absorb the carbon dioxide formed at the steel : gas surface, because of the high dissociation pressure of the carbonate. In Group II are listed those carbonates known to be effective catalysts, and without exception they are characterized by low dissociation pressures.

In Group III are listed those reactions involved in the carburization of steel and the conversion of carbon dioxide to carbon monoxide. The column headed Δp gives the difference between the carbon dioxide pressure for reaction No. 9 and the reaction in question. If the Δp value is greater than that shown for reaction No. 8 (the case where carburization occurs in the absence of a catalyst), the presence of the metallic oxide speeds up the conversion of carbon dioxide into carbon monoxide.

It should be indicated that the values in Table II may only be used as a qualitative guide. The percentage accuracy of the data is not sufficiently great to warrant a quantitative use of the figures. Note, for example, the wide range of carbon dioxide pressures for reaction No. 9. The data from Johansson and Von Seth and Takahashi indicate that austentite can be carburized to its saturation value at 900 degrees Cent. (1650 degrees Fahr.) by pure carbon in the

presence of carbon monoxide and carbon dioxide. The data of Becker and of Bramely and Lord indicate that saturation cannot be achieved at 900 degrees Cent. (1650 degrees Fahr.) under those conditions. Regardless of these differences, however, the data do show that the presence of a metallic oxide formed from a carbonate having a low dissociation pressure will accelerate the removal of carbon dioxide by increasing the partial pressure differential, $\triangle p$.

It is believed that the foregoing explanation of the mechanism of the catalytic effect is in harmony with the experimental results of this investigation. The experimental work demonstrated that in the case of sodium carbonate and barium carbonate, a reaction occurred with carbon at temperatures below those at which direct dissociation of the carbonate could occur. No such reaction was observed with calcium carbonate. The above outlined theory is in accordance with the observed fact that the decomposition of the carbonate catalyst does not occur to a progressively greater degree till decomposition is complete, but instead, that the percentage decomposition levels off to a fixed value, dependent upon the catalyst and the temperature employed.

ACKNOWLEDGMENT

The writers wish to express thanks for financial support received from the Wisconsin Alumni Research Foundation.

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## DISCUSSION

**Written Discussion:** By Hugh Rodman, Rodman Chemical Co., Verona, Pennsylvania.

The authors have shown the presence of small amounts of carbonates in carburizing compounds at 930 degrees Cent. (1700 degrees Fahr.). They do not, however, support the old belief that carburization requires a slow release of $CO_2$ from these carbonates.

The action of the carbonates seems well established. They supply intimately

mixed alkaline oxide catalysts within the carbon sponge and these oxides help the carbon in some way to reduce $CO_2$ to CO.

It is noted that even if no carbonates were supplied by the original mixture some would probably be formed by reaction between the $CO_2$ developed at the steel surface and the alkaline oxides in the carbon. It is easily possible that all reduction of $CO_2$ to CO occurs through an intermediate carbonate stage.

Apparently carburization by means of compound consists of a cycle of reactions employing two catalysts. The steel itself is the first catalyst and helps to break down CO to $CO_2$ and carbon. The steel accepts the carbon if it can, otherwise it remains on the steel surface as a sort of soot. The alkaline oxide is the second catalyst and helps the carbon to reduce the $CO_2$ to CO, possibly by means of a carbonate reaction.

**Written Discussion:** By G. C. Williams, associate professor of chemical engineering, University of Louisville, Louisville, Ky.

This paper by T. C. Fong and R. A. Ragatz is a timely and meaty contribution. The use of carburizing compounds, accelerators, addition agents, etc., is definitely still in the art stage and until more information is presented in the manner of this article, the technologist will still be guessing.

The negative values of $CO_2$ absorption are most interesting, although the percentage figures must be recalculated to give a full appreciation of their significance. Using 90 gram charcoal as a base and considering the $BaCO_3$ runs at 650 and 700 degrees Cent. (1200 and 1290 degrees Fahr.):

$$\text{Total } CO_2 \text{ present must be } \frac{44.01}{197.37} \times \frac{10}{0.602} = 3.71 \text{ grams.}$$

$$CO_2 \text{ present in } BaCO_3 = \frac{44.01}{197.37} \times 10 = 2.23 \text{ grams.}$$

$$\text{Present in 90 grams carbon} = 1.48 \text{ grams.}$$

On the basis of Fig. 3, at 650 and 700 degrees Cent. (1200 and 1290 degrees Fahr.) on 7 hours' exposure the net gain was about 4 per cent or 0.148 gram. If the carbon alone was considered, by Fig. 1, under the same conditions (excepting presence of $BaCO_3$), the pickup would be about 15 per cent or 0.22 gram. This indicates a loss in pickup due to the presence of $BaCO_3$, or it may be the same pickup by the carbon, but with an evolution from the $BaCO_3$ similar to that postulated for the $Na_2CO_3$.

In the case of the $CaCO_3$, 7 hours at 650 and 700 degrees Cent., a similar calculation may be made. (90 g. C. basis.)

$$\text{Total } CO_2 \text{ present} = \frac{44.01}{100.09} \times \frac{10}{74.9} = 5.88 \text{ grams.}$$

$$\text{Present in } CaCO_3 = \frac{44.01}{100.09} \times 10 = 4.40 \text{ grams.}$$

$$\text{Present in carbon} = 1.48 \text{ grams.}$$

but from Fig. 4 the final value was about 3 per cent or a pickup of about 0.176 gram as against a value of 0.22 gram by Fig. 1 for the charcoal conditions. The same conclusions may again be stated, i.e., either a drop in pickup was caused by the presence of the carbonate or an evolution of $CO_2$ from the carbonate masked the true pickup by its disappearance.

I feel that the authors have been very conservative on their conclusions on this portion of the article.

In Part III the action of the various catalysts may be compared further in an interesting manner if the matter is studied from the steel side as well as from the gas side. The mechanism of case hardening is considered to be a combination of carbide formation at the surface of the austenitic steel with a diffusion action following closely and directly. At any instant, therefore, the carburizing medium must act on a partially saturated austenite.

In the experiments reported by this paper, comparisons were made on an overall basis, i.e., weight rate change on a constant time, constant temperature basis, and the figures for carburizing with catalytic agents showed to decided advantage. This is technically and practically true. However, if it may be assumed that the carbon gradient in the austenite is relatively constant and independent of the catalytic agent, then the surface concentration would be relatively the same at the condition of constant weight increase. Rates of increase, taken at the same weight increase, and temperature points would therefore correspond to the relative instantaneous catalytic effect.

On this basis, by Figs. 8 and 9, the catalysts would show greater activity than the authors conclude. Furthermore, the rate of increase for $Na_2CO_3$ and $BaCO_3$ would be approximately equal.

On the foregoing basis, the constancy of slope for catalyzed carbon increases may be accounted for. The carbon diffusivity into the steel should be constant if the driving force (i.e. carbon differential) is constant from metal surface in. The metal surface composition should be constant if the gas phase composition is constant and if the carbon diffusion rate is fixed. And to complete the picture, the gas phase composition can only be constant if cyclic or equilibrium conditions prevail. The gas evolution theory for a compound at constant temperature cannot fulfill this condition; the oxide or metal cycle can.

**Written Discussion:** By E. G. Mahin, professor of metallurgy and head, Department of Metallurgy, University of Notre Dame, Notre Dame, Ind.

In the authors' discussion of the action of sodium carbonate as an energizer it is stated that carbon exerts a reducing action, with the formation of elementary sodium and carbon monoxide. This suggestion seems somewhat surprising, in view of the thermochemistry involved, especially at a temperature as low as 750 degrees Cent. (1380 degrees Fahr.). 1 do not mean to argue that this action does not take place but the similarity of curves shown in Figs. 2 and 3 would appear to make such an assumption unnecessary unless the reaction indicated by the equation on page 170 of the paper has been shown, by other evidence, to take place.

In general conclusion No. 4, it is stated that my earlier observation that oxides and hydroxides added to a carburizing compound will revert to carbonates on heating was verified, but that my assertion that barium carbonate, especially, releases its carbon dioxide slowly at higher temperatures was not verified. I would remark here that in the papers quoted I was more especially directing attention to the fact that the observed energizing action of oxides and hydroxides is not incompatible with the generally accepted view as to the mechanism of carbonate energizing action, rather than to any definite statement regarding the rate of carbon dioxide evolution.

It should be noted also that the "leveling off" of the curves representing carbon dioxide evolution with respect to time should not lead to the conclusion

that the usefulness of the energizer ceases as soon as the curve reaches its horizontal portion. It should be remembered that a very important function of the energizer is the early expulsion of nitrogen from the carburizing box, replacing this gas with carbon dioxide and, later, carbon monoxide. After this has been accomplished a very minor evolution of gas should be sufficient to obstruct back diffusion of nitrogen through crevices in the luting of a carefully prepared box.

**Written Discussion:** By George M. Enos, lieutenant colonel, Ordnance Department, War Department, Cincinnati, Ohio.

The authors are to be congratulated on adding to the literature on the mechanism of carburization some interesting data presented in a way that is easily followed.

It is noted that "plain charcoal" was used as a basis of comparison for various components. This is a logical method of attack, but a note of caution is in order. Charcoal contains mineral matter, which presumably acts as a catalyst. Charcoals obtained from different forests almost certainly have different mineral matter. Therefore, the comparisons are with a particular charcoal, not with charcoal in general.

Some years ago, the writer had occasion to use pure sugar carbon as a basis for formulating carburizing compounds for experimental work. The evidence at that time led to the conclusion that without catalyst addition, there was no carburization. It would be interesting to know whether the data plotted in Figs. 8 to 11 for $Na_2CO_3$ and $BaCO_3$ additions would be the same if pure carbon had been the base instead of the charcoal that was used. It would also be interesting to know the actual analysis of the charcoal as to mineral content and the analysis of the minerals.

## Oral Discussion

C. T. Patterson:[1] I want to know if you will give an opinion on strontium compounds and lithium compounds as carburizers.

M. A. Scheil:[2] I would like to ask Professor Ragatz if he analyzed for nitrogen in making these gas analyses of the $CO : CO_2$ reaction. Have you found any nitrogen present during the carburizing reaction and, if so, whether that had any effect upon these reactions?

L. W. Hudson:[3] We had an experience with carburization that was unique to me. We had a selective carburized job which was copper plated and carburized satisfactorily in our own plant.

The job was then turned over to a sub-contractor who immediately experienced difficulty in carburizing. Experiments showed that hardness, after carburizing and quenching, fell off appreciably ⅛ inch from the edge of the copper plating and fell off considerably 1/16 inch from the copper plating. A different commercial compound was tried and the trouble cleared up at once.

Not being an expert on carburizing I wondered if perhaps someone more experienced might be able to explain why one compound worked successfully while the other would not.

[1]Metallurgical engineer, The Solvay Process Co., Syracuse, N. Y.
[2]Director of metallurgical research, A. O. Smith Corp., Milwaukee, Wis.
[3]Assistant chief metallurgist, Goodyear Aircraft Corp., Akron, Ohio.

H. B. KNOWLTON:[4] I would like to ask the authors a question concerning the action of chemical energizers. A number of years ago when I started working on carburized compounds, the question arose as to whether the action of chemical energizers was a catalytic one or not, and whether a contact between the energizers and the carbon particles was necessary.

It seemed to us that the simplest way to determine this would be to make a test, packing some of the boxes in such a way that the chemical energizer and the charcoal were separated, and packing other boxes with a compound containing energizers and charcoal in contact. The former was done by placing carbonate in the bottom of the container and supporting the charcoal above by means of two wire screens which would assure that the chemical and the charcoal did not come in contact with each other.

Test pins were placed in the carbonate and in the charcoal at various distances above the carbonate. The test pin in the carbonate showed little or no carburizing. The most vigorous carburizing occurred in the case of the pin in the charcoal just above the carbonate. The pins at higher levels in the charcoal showed less effect of carburizing. In the case of the box packed with an ordinary compound the carburizing action was fairly uniform from top to bottom.

It seems to us that carburizing is accomplished by CO in contact with the steel. If the conditions in the carburizing container are such that the atmosphere in contact with the steel is largely CO, the maximum carburizing action should take place. However, the reaction of CO with the steel produces $CO_2$, which inhibits carburizing. Consequently it is necessary that the $CO_2$ be immediately reconverted to CO by contact with charcoal or some chemical, such as sodium, barium, or calcium compounds. We have run experiments with varying amounts of chemical energizers mixed with charcoal, and have found little difference in the carburizing action between 4 and 20 per cent sodium carbonate, or between 8 and 20 per cent barium carbonate.

We believe that if the compound is successful in maintaining an atmosphere of CO in the carburizing container this is all that the compound can do.

I would like to ask the authors if they have ever tried physically separating the chemical energizers from the carbon.

### Authors' Reply

The authors wish to thank Mr. Rodman for the comments he offers regarding the experimental results and the theory proposed to explain the action of the catalysts.

Dr. Williams suggests that some conclusions regarding the decomposition of the catalyst at 650 and 700 degrees Cent. (1200 and 1290 degrees Fahr.) may be drawn if the results with plain charcoal (Fig. 1) are compared with the results obtained when using the barium carbonate catalyst (Fig. 3) and those obtained when using the calcium carbonate catalyst (Fig. 4). If it is postulated that the charcoal in the catalyzed mix exhibits exactly the same pickup of carbon dioxide as the uncatalyzed charcoal, the figures presented in Dr. Williams' discussion would indicate a percentage decomposition of 3.3 for the barium carbonate and 1.0 for the calcium carbonate. Dr. Williams of necessity based

[4]Materials engineer, Engineering Department, International Harvester Co., Chicago.

his calculations on values scaled from relatively small graphs. The more accurate data, taken directly from tables of original data not presented in this paper, yield values of 1.6 for the percentage decomposition of barium carbonate and 1.0 for the percentage decomposition of calcium carbonate. These low values approach the limit of accuracy of the experimental work. The authors, in the preparation of their paper, did consider the advisability of including tables for percentage decomposition of catalyst, based on the assumption that the charcoal in the catalyzed compound behaved exactly as did the uncatalyzed charcoal. However, they concluded that it would be inadvisable to do so in view of the uncertainties involved in assuming the adsorptive capacity of the charcoal to be unaffected by the presence of the catalyst. The writers are interested to note that Dr. Williams' somewhat different interpretation of Figs. 8 and 9 also lead him to the conclusion that the catalytic activity exerted by the sodium carbonate and by the barium carbonate is sustained, and that there is no ultimate exhaustion of the catalytic activity.

Professor Mahin raises some points with respect to the reaction between carbon and sodium carbonate, particularly with respect to the possibility of securing reduction to sodium. It is quite true that the present writers offer no direct evidence that reduction to the metal state occurred in their experiments. However, it may be pointed out that prior to the development of the Hall electrolytic process for producing aluminum, large quantities of sodium were manufactured for use as a reducing agent for aluminum chloride, and that the sodium made for this purpose was produced by heating sodium carbonate or sodium hydroxide with carbon in iron retorts, thus forming sodium vapor which was drawn off and condensed. Thus, the reaction suggested as occurring when carburization is carried out with a compound catalyzed with sodium carbonate was actually used in the past to produce large quantities of sodium. Furthermore, it should be pointed out that the reaction in question was studied by individuals interested in the development of catalysts for increasing the rate of formation of producer gas or of water gas. For example, the work of Fox and White[5] at the University of Michigan and that of Kröger and Fingas[6] in Germany may be cited. These investigators have arrived at the conclusion that the reduction of sodium carbonate to metal does occur and is one of the factors involved in the catalytic effect exerted by sodium carbonate in the formation of producer or water gas. Professor Mahin indicates that his doubts as to the possibility of the reaction occurring at 750 degrees Cent. (1380 degrees Fahr.) are based upon the thermochemistry involved. The writers regret that Professor Mahin did not see fit to amplify this point, as they are unaware of thermochemical factors militating against the reaction occurring. Professor Mahin points out the desirability of eliminating nitrogen from the carburizing retort and suggests that this is one of the useful roles played by the catalyst. While this conclusion certainly is sound, it would be interesting to obtain some quantitative data along this line.

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[5]D. A. Fox and A. H. White, "Effect of Sodium Carbonate Upon Gasification of Carbon and Production of Producer Gas," *Industrial and Engineering Chemistry*, Vol. 23, 1931, p. 259.

[6]Kröger and Fingas, "Die Einwirkung von Kohlenstoff und Alkalicarbonate," *Zeitschrift für Anorganische u. Allgemeine Chemie*, Vol. 212, 1933, p. 269.

Colonel Enos very properly points out that the nature of the carbonaceous base has an influence on the carburizing results. The charcoal selected for the work described by the authors is used by at least one large manufacturer of commercial carburizing compounds, hence it was considered to be suitable for the present investigation. Colonel Enos asks whether, in the writers' opinion, the curves plotted in Figs. 8 to 11 would be altered if a different carbonaceous base had been used. It is the writers' definite opinion that these curves would be very materially affected if different carbonaceous substances were used. Experimental data presented in an earlier paper by one of the present writers[7] definitely showed that when using a given catalyst, the nature of the carbonaceous base still is a factor that influences the rate of carburization. While the curves of Figs. 8 to 11 would be shifted by changing the carbonaceous base, the writers nevertheless are of the opinion that the new curves would also show a sustained catalytic activity. Colonel Enos expresses interest in the mineral analysis of the charcoal. While we do not have a specific mineral analysis for the lot of material used in the present investigation, the laboratories of the Tennessee Eastman Corporation very kindly furnished the following data, which may be regarded as representative for the material employed. It was stated in their report that the charcoal was made from Appalachian hardwoods, mostly from oak and maple.

| | | | |
|---|---|---|---|
| Per Cent Ash | | | 1.5 per cent |
| Analysis of Ash: | | | |
| $K_2O$ | = 44.0 per cent | $Fe_2O_3$ | = 3.2 per cent |
| $Na_2O$ | = 1.5 per cent | $P_2O_5$ | = 2.8 per cent |
| CaO | = 26.8 per cent | $SO_3$ | = 13.1 per cent |
| MgO | = 2.8 per cent | $SiO_2$ | = 5.8 per cent |

In answer to Mr. Patterson's question, we should like to state that a number of years ago one of the present authors[8] carried out an extensive investigation on the use of a wide variety of catalytic compounds. This investigation showed that strontium carbonate was an effective catalyst. Lithium carbonate was also effective, but the results were somewhat obscured by the fact that there was surface attack on the steel samples. In the case of strontium carbonate, there was no surface attack of the steel samples.

Mr. Scheil raised the question as to whether any nitrogen analyses were made. We regret to say that no such analyses were performed. In evaluating the evolution of carbon dioxide from the compound, we did not analyze the gases that were issuing, but based the entire work on analyses of the residual compound left after the heat treatment. That is, the used compounds were analyzed for the carbon dioxide which was not driven off and the gases emerging were not analyzed in any way.

With respect to the question Mr. Hudson raised regarding the inability of a certain compound to carburize up to the copper plate, we regret to state that we have no particular comment or suggestion to offer along those lines. Perhaps some metallurgist acquainted with the practical aspects of carburization would be able to answer this question.

Mr. Knowlton describes an interesting experiment wherein the catalyst and carbonaceous substance were sharply separated. The results reported by Mr. Knowlton are in harmony with the theory advanced by the authors of this paper

[7]Reference 17 in the Bibliography.

[8]Reference 15 in the Bibliography.

to explain the catalytic effect of sodium and barium carbonate. According to this theory, it would be highly important that the catalyst be intimately mixed with the carbonaceous substance. Any sharp separation of the two would certainly result in failure of the catalytic effect coming into play. Samples imbedded in the charcoal would be expected to exhibit the degree of carburization obtainable in a carburizing box containing charcoal alone. The higher rate of carburization reported by Mr. Knowlton as occurring in the charcoal just above the carbonate layer might possibly have been caused by a small amount of charcoal powder sifting through the screen, onto the upper part of the carbonate layer, thus permitting the establishment of the cyclic reactions postulated in this paper, in the upper part of the catalyst layer and in the lower part of the charcoal layer. The writers of the present paper, however, have carried out no experiments of the type described by Mr. Knowlton.

# THE ISOTHERMAL TRANSFORMATION OF CASE-CARBURIZED S.A.E. 4815

By J. R. Cruciger and J. R. Vilella

*Abstract*

*In order to provide a complete map of the isothermal transformation of case-carburized S.A.E. 4815 steel it is necessary to work out the diagram both for the carburized case and the uncarburized core. The diagrams, together with representative photomicrographs are presented and compared. The diagram for the core represents the lowest carbon S.A.E. steel so far investigated by this method in the laboratory at which this work was done. The manner in which the structure is influenced by the previous separation of the proeutectoid constituent is discussed, and a possible explanation of the origin of the structure called "X constituent" in a previous publication by Davenport is offered.*

THE isothermal transformation diagram of S.A.E. 4815 uncarburized represents the behavior of the core when the steel is case-carburized for service; but from this diagram it is not possible to predict, or even to guess intelligently, the behavior of the carburized case under any set of conditions of temperature and time. If a complete and accurate map of the isothermal transformation of this steel in the condition normally used in service is to be had, the isothermal diagram of the carburized case must also be determined. Such a diagram has been worked out and is given in Fig. 1. For comparison, the diagram of the uncarburized steel is given in Fig. 2, and both diagrams, combined in a single plot, in Fig. 3.

While the combined isothermal diagrams shown in Fig. 3 and the accompanying photomicrographs constitute the best summary of this work, it may be added by way of conclusion that: 1) the effect of carbon in this alloy steel parallels closely a similar effect previously observed in plain carbon and other alloy steels; 2) the fact that at temperatures below 1000 degrees Fahr. (540 degrees Cent.) no

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separation of proeutectoid ferrite occurs in the low-carbon steel prior to the transformation of austenite to a carbide-ferrite aggregate, may explain why the structures formed by isothermal transformation in this temperature range consist of an acicular, ferrite-rich aggregate, sometimes referred to as the "X" constituent; 3) except for a radical change in the shape of the line representing the beginning of the separation of the proeutectoid constituent, and for a marked lowering of the martensite point, the addition of carbon does not seem to alter the general shape of the transformation curve, but it does very markedly retard the transformation at the lower temperature levels, in conformity with previous experience on other steels.

*Steel Used.* The analysis of the uncarburized heat of S.A.E. 4815 and that of the carburized portion used in this work is as follows:

| | C | Mn | Si | Ni | Mo |
|---|---|---|---|---|---|
| Uncarburized steel | 0.16 | 0.52 | 0.27 | 3.36 | 0.19 |
| Carburized case; band 0.004-0.012 inch from edge | 0.97 | — | — | 3.36 | 0.20 |

Since no appreciable change occurred in the significant alloying elements, nickel and molybdenum, as a result of the carburizing treatment, the difference between the two diagrams may be attributed entirely to the difference in carbon content.

*Carburizing Treatment.* Two methods of obtaining suitable specimens for this work were considered: 1) carburization of thin specimens throughout, and 2) case-carburization of bars of the steel (⅝ inch square x 4½ inches long) from which suitable specimens, $\frac{3}{32}$ inch thick, could be cut. The second method was adopted for the following reasons: 1) the presence of a carbon gradient lends itself nicely to the study of the effect of carbon on the rate of transformation; 2) the case-carburizing treatment approximates commercial practice more closely than total carburization of a thin specimen; and 3) a case of sufficient depth to permit adequate microscopic examination could be obtained in a reasonably short carburizing time (18 hours at 1700 degrees Fahr.). The carburization was carried out in a commercial pack-carburizing compound, and the material was furnace cooled to room temperature in the carburizing box.

*Austenitizing Treatment.* An austenitizing temperature 100 degrees Fahr. higher than the carburizing temperature was used in order to insure complete solution of the carbide in a short time;

trial specimens showed that this could be accomplished in 20 minutes at 1800 degrees Fahr. (980 degrees Cent.). This treatment was adopted for the determination of the isothermal transformation diagram; the resulting austenite grain size was No. 7 A.S.T.M.

To minimize decarburization during the austenitizing and transformation treatments all specimens were rather heavily copper-plated.

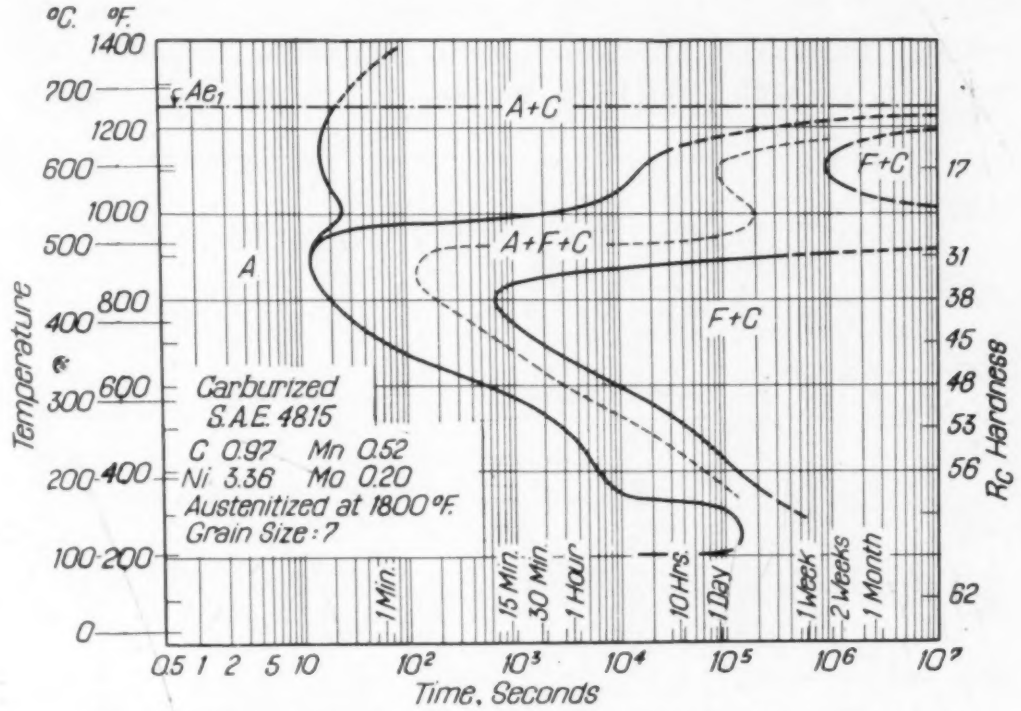


Fig. 1—Isothermal Transformation Diagram of Steel S.A.E. 4815 As Carburized.

This precaution proved to be worthwhile, as some of the preliminary specimens, which were not copper-plated, decarburized markedly, particularly during the long periods at the higher transformation temperatures.

In comparing the isothermal diagrams obtained before and after carburization it must be borne in mind that the austenitizing temperature used in working out the diagram of the uncarburized steel was 1650 degrees Fahr. (900 degrees Cent.), which yielded an austenite grain size of 8-9 A.S.T.M. While it is true that an increase in austenite grain size generally acts similarly to an increase in carbon or alloy content—that is, it displaces the upper portion of the isothermal curve to the right—in this particular instance this effect was negligible, as was verified by comparison of results on the core of the carburized specimen with those previously obtained on

the uncarburized steel. For this reason, and because the isothermal diagram of the uncarburized steel includes more accurately determined points than could be obtained from the core of the carburized specimens, it was adopted for this comparison.

*The $Ae_1$ and Martensite Points.* The $Ae_1$ determined by metallographic and hardness methods, was found to be 1250 ± 10 degrees Fahr. (675 degrees Cent.). The martensite point, which is the highest temperature of instantaneous martensite formation on quenching, was determined by the method of Greninger and Troiano[1],

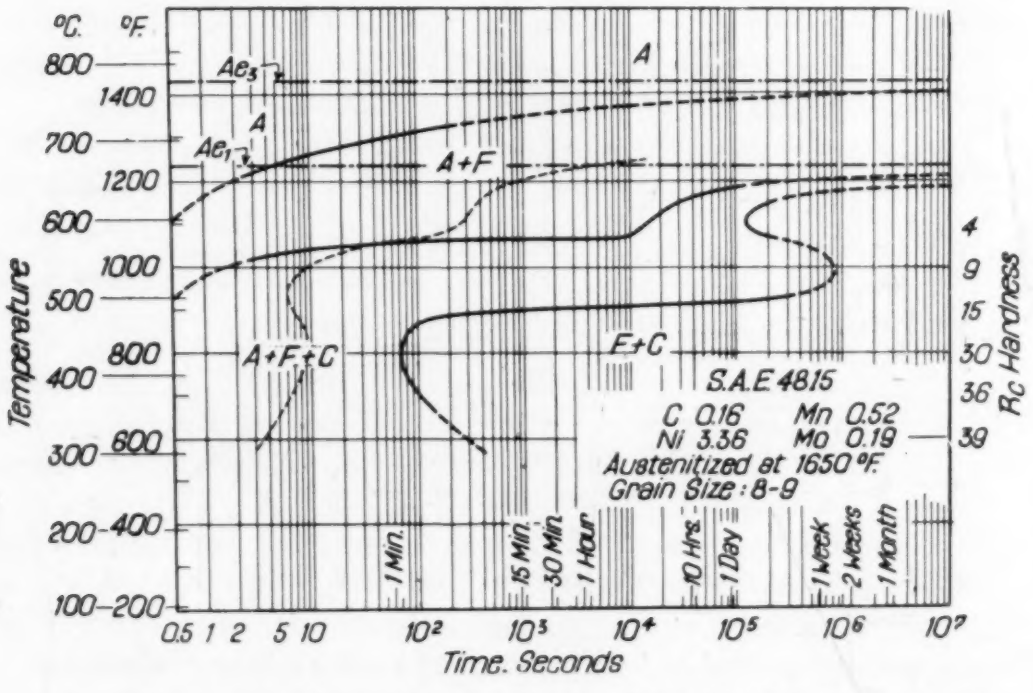


Fig 2—Isothermal Transformation Diagram of Steel S.A.E. 4815 Before Carburization.

that is, by quenching a series of small specimens for 30 seconds at appropriate successively lower temperatures, followed by tempering 2 minutes at 600 degrees Fahr. (315 degrees Cent.). The first evidence of tempered martensite, which indicates that the martensite point has been located, was found in the specimen quenched in a bath at 200 to 205 degrees Fahr. (95 degrees Cent.).

*Effect of Carbon on the Isothermal Transformation Diagram.* It will be noticed in Fig. 3 that the main effect of carburization is to retard the rate of transformation, that is, the pair of curves for

[1]A. B. Greninger and A. R. Troiano, "Kinetics of the Austenite to Martensite Transformation in Steel", TRANSACTIONS, American Society for Metals, Vol. 28, 1940, p. 537-574.

beginning and ending of transformation in the carburized-case lie to the right of the corresponding pair for the uncarburized steel, particularly at the lower temperature levels; this is quite typical of the effect of carbon in plain carbon and alloy steels. However, at 1100 degrees Fahr. (595 Cent.) and above, the curves for beginning

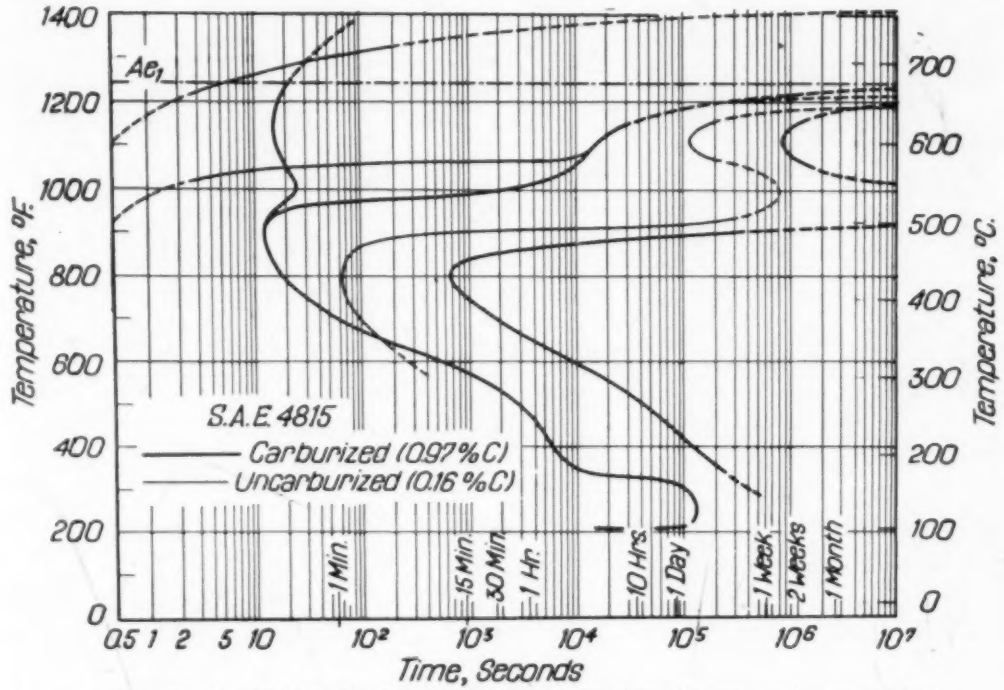


Fig. 3—Comparison of Isothermal Transformation Diagrams of Steel S.A.E. 4815 Before and After Carburization.

of transformation to pearlite in both the carburized and uncarburized steels very nearly coincide; the reason for this will become apparent when the structure formed at this temperature is discussed. As to vertical displacement, it will be observed that though the curves for the uncarburized steel lie above the corresponding curves for the carburized steel, the "knee" occurs at approximately the same temperature. The curve depicting 50 per cent transformation, shown as a thin dashed line in Figs. 1 and 2 was omitted in Fig. 3 in order to keep this diagram as simple as possible.

## Comparison of Microstructure

In order to insure that the portion of the carbon gradient studied did not include decarburized metal or other surface effects, metallographic examination was made, in all cases, on a band 0.004 to

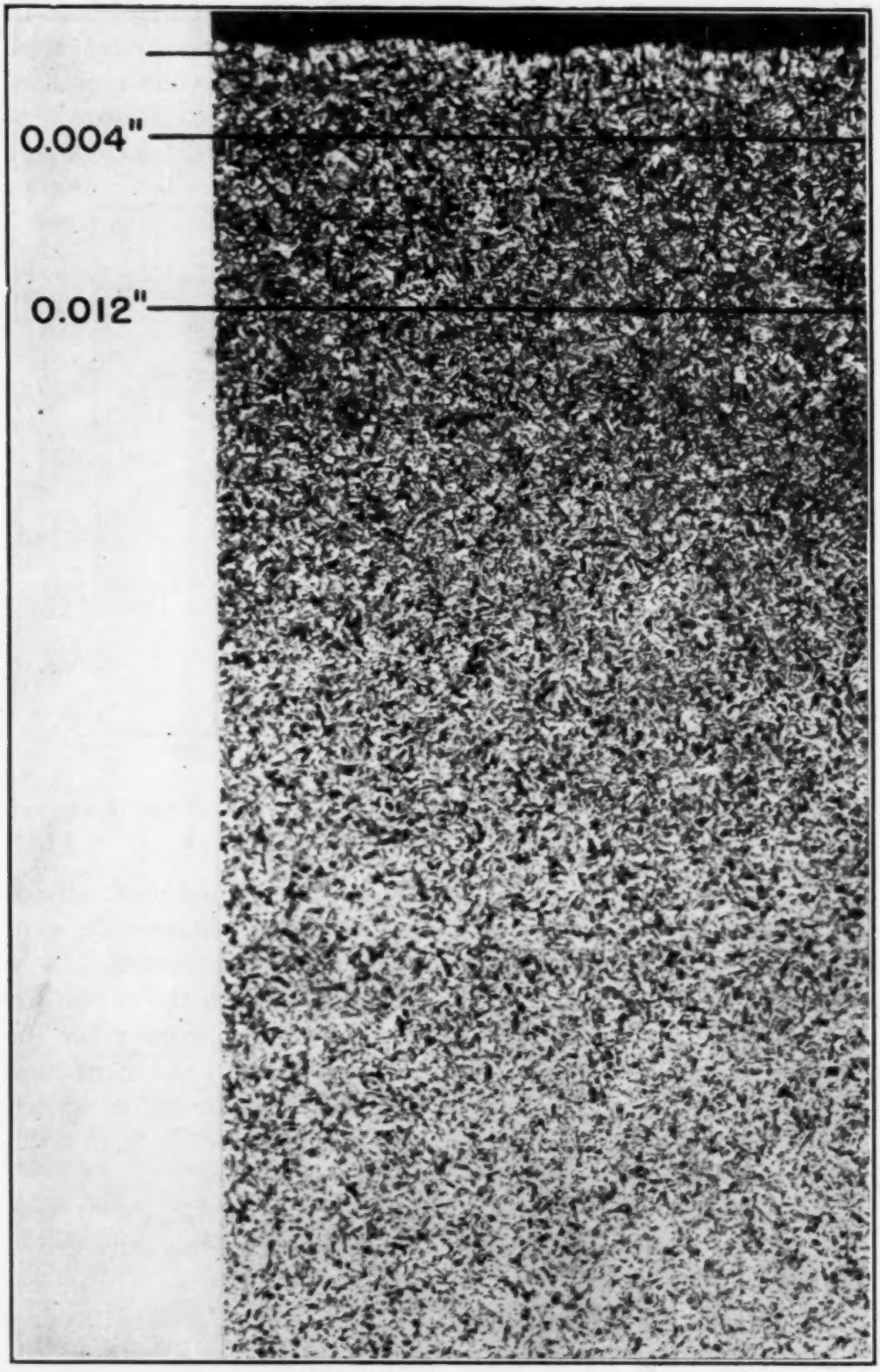


Fig. 4—Portion of Carburized Specimen Used to Obtain Transformation Diagram, Photomicrographs and Chemical Analysis. 4 Per Cent Picral. × 100. Zone from Surface to 0.004 Inch Disregarded. Zone from 0.004 to 0.012 Inch Used to Obtain Transformation Diagram, Photomicrographs and Millings.

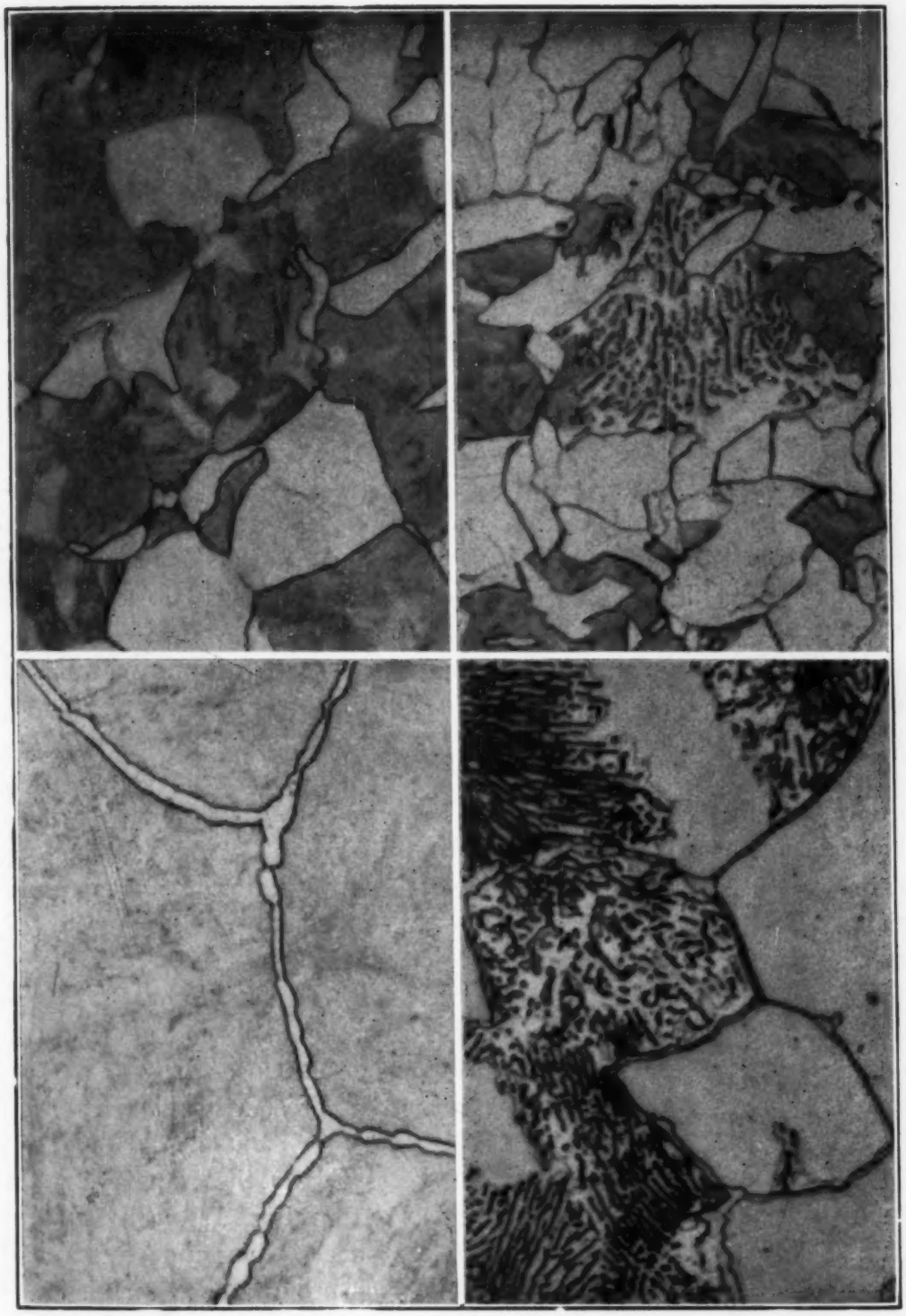

Fig. 5A—Upper.
Fig. 5B—Lower.

Fig. 6A—Upper.
Fig. 6B—Lower.

Figs. 5 and 6—Effect of Carburization on the Structure of S.A.E. 4815. (A) Uncarburized (0.16 Per Cent Carbon). (B) Case-Carburized (0.97 Per Cent Carbon). Fig. 5—Transformation Temperature 1200 Degrees Fahr. Fig. 6—Transformation Temperature 1100 Degrees Fahr. All Specimens Picral Etched. × 2000.

0.012 inch from the edge, as shown in Fig. 4. The millings for chemical analysis and the photomicrographs were also obtained within this band.

Fig. 5 shows the product of the proeutectoid reaction at 1200 degrees Fahr. (650 degrees Cent.) in the (A) uncarburized, (B) carburized steel. The background in both is martensite; the proeutectoid constituent is ferrite in the uncarburized but carbide in the carburized specimen. The marked difference in appearance of the martensite is due to the fact that in the uncarburized specimen it is rather low carbon, because the separation of proeutectoid ferrite is only partially completed; on the other hand, in the carburized specimen the martensite is of eutectoid, or higher, carbon content.

Fig. 6 illustrates the structure of specimens partially transformed at 1100 degrees Fahr. (595 degrees Cent.). At this temperature level the separation of proeutectoid carbide and of proeutectoid ferrite in the carburized and uncarburized specimens respectively is substantially completed before the transformation of the remaining austenite to a carbide-ferrite aggregate begins. The austenite which then is still untransformed is, therefore, of eutectoid composition in both; consequently, when it transforms eventually, the resulting structure is, in both instances, a very similar carbide-ferrite aggregate. (See Fig. 6.) Moreover, since the composition of the untransformed austenite in both the carburized and uncarburized specimens is the same after the separation of the proeutectoid constituent, the time for beginning of transformation at one common temperature level is also the same. This explains why the curves representing beginning of transformation to pearlite in both steels (Fig. 3) practically coincide between 1100 degrees Fahr. (595 degrees Cent.) and the $Ae_1$. On the other hand, the curves for the ending of transformation do not coincide because the volume of austenite in the carburized far exceeds that present in the uncarburized steel.

At 1000 degrees Fahr. (540 degrees Cent.) the transformation product of the uncarburized steel, shown in Fig. 7A, can best be described as rather coarse and widely separated carbide spheroids in a matrix of ferrite. Similar spheroids occur in the corresponding carburized specimen (Fig. 7B) but in addition there are large blocks of a structure resembling pearlite, made up of closely spaced and rather rectilinear lamellae. In this specimen there is still a thin, but well defined, network of proeutectoid carbide.

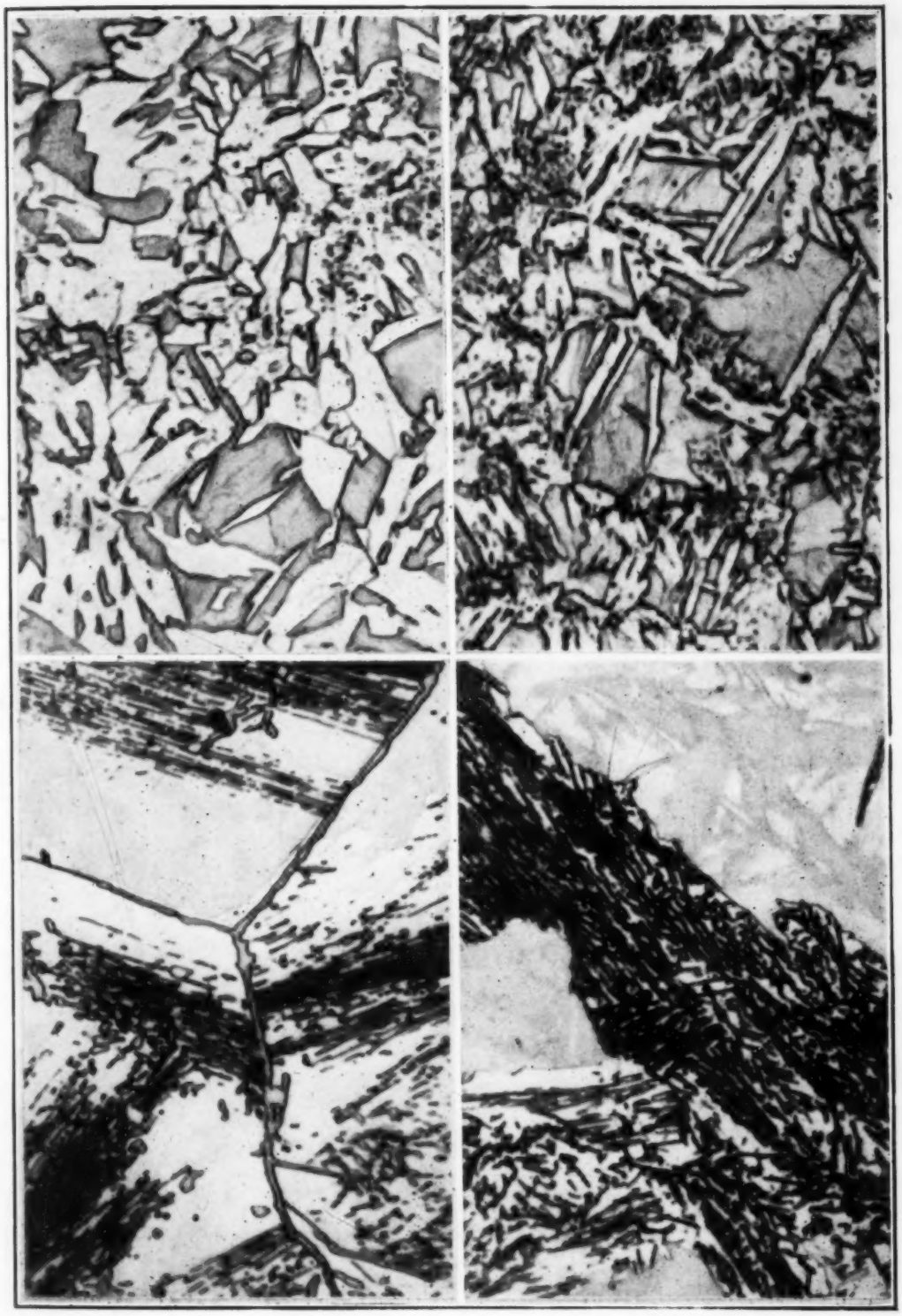

Fig. 7A—Upper.
Fig. 7B—Lower.

Fig. 8A—Upper.
Fig. 8B—Lower.

**Figs. 7 and 8—Effect of Carburization on the Structure of S.A.E. 4815. (A) Uncarburized (0.16 Per Cent Carbon). (B) Case-Carburized (0.97 Per Cent Carbon). Fig. 7—Transformation Temperature 1000 Degrees Fahr. Fig. 8—Transformation Temperature 900 Degrees Fahr. All Specimens Picral Etched. × 2000.**

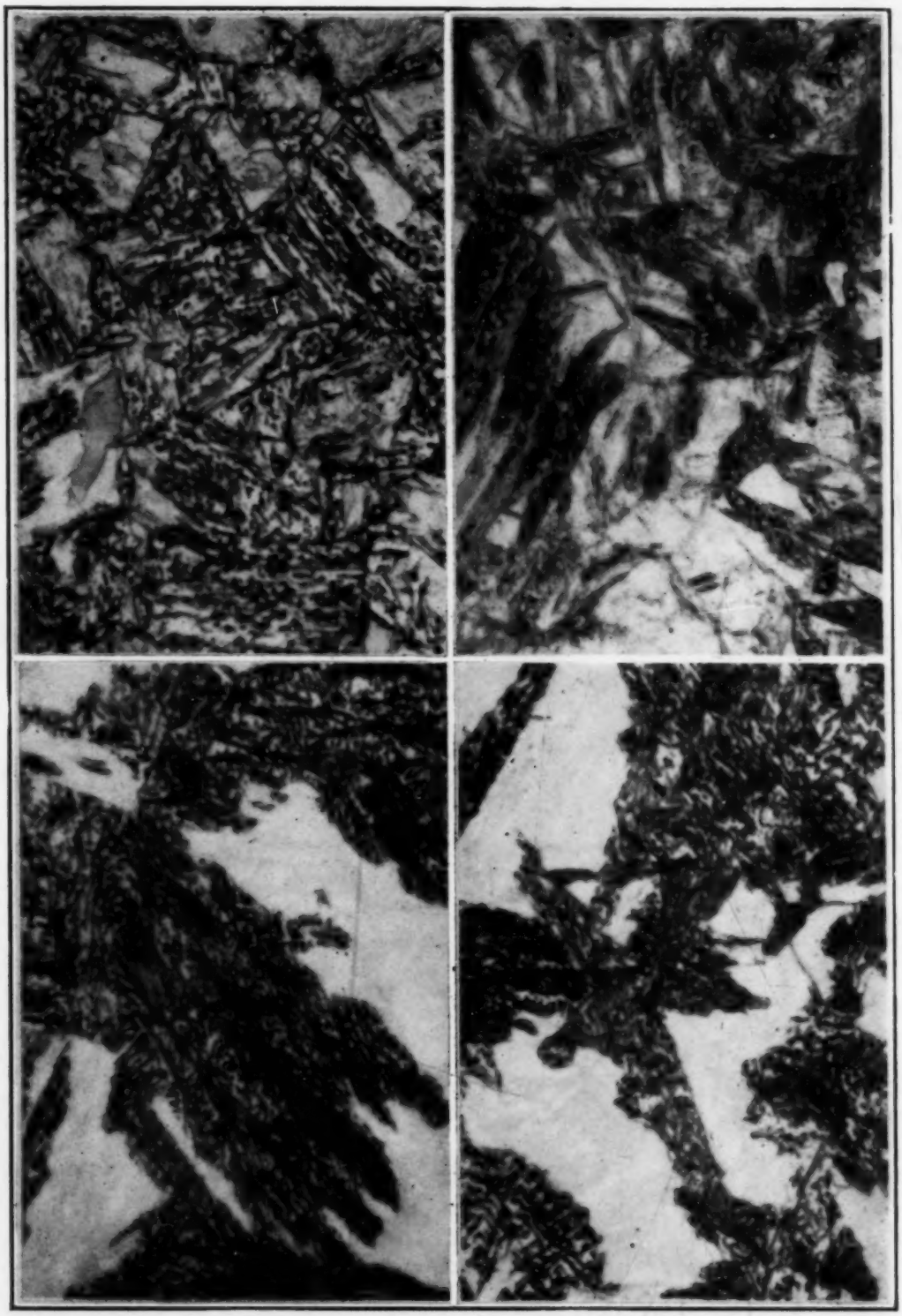

Fig. 9A—Upper.
Fig. 9B—Lower.

Fig. 10A—Upper.
Fig. 10B—Lower.

**Figs. 9 and 10—Effect of Carburization on the Structure of S.A.E. 4815. (A) Uncarburized (0.16 Per Cent Carbon). (B) Case-Carburized (0.97 Per Cent Carbon). Fig. 9—Transformation Temperature 800 Degrees Fahr. Fig. 10—Transformation Temperature 700 Degrees Fahr. All Specimens Picral Etched. × 2000.**

At 900 degrees Fahr. (480 degrees Cent.), the separation of proeutectoid constituent prior to the transformation of austenite to a carbide-ferrite aggregate does not occur as a separate process in either the carburized or uncarburized steel. Therefore, in the carburized steel it is an austenite containing 0.97 per cent carbon which eventually transforms, whereas in the uncarburized steel the austenite contains only 0.16 per cent carbon. Under these conditions it is understandable that the structure formed at this temperature level should differ so markedly in appearance, as shown in Figs. 8A and 8B. In the carburized steel the structure is an aggregate which in appearance resembles both pearlite and coarse bainite; in the uncarburized steel it consists of more or less acicular areas of ferrite sprinkled with finely divided carbide particles. This latter structure, which has been called "X" constituent in a previous publication,[2] probably appears when proeutectoid ferrite is prevented from separating by rapid cooling to a comparatively low temperature but subsequently is given an opportunity to separate out at constant temperature. Under these conditions the ferrite which eventually separates is presumably supersaturated with carbon, which precipitates in the form of minute particles when the steel is held at temperature for sufficient time.

The 800 degrees Fahr. (425 degrees Cent.) structure of the uncarburized specimen, Fig. 9A, is of the same general type as the 900 degrees Fahr. (480 degrees Cent.), but contains more carbide particles within the ferrite needles; that of the carburized specimen, Fig. 9B, is likewise similar to that at 900 degrees Fahr. (480 degrees Cent.) but somewhat more acicular and denser, i.e., it is more difficult to resolve under the microscope than the 900 degrees Fahr. (480 degrees Cent.) product.

In the 700 degrees Fahr. (370 degrees Cent.) structure of the uncarburized specimen, Fig. 10A, the carbide precipitation within the ferrite needles is so heavy that the needles have completely lost their ferritic appearance; this structure, therefore, may be considered a typical low carbon bainite rather than an "X" structure although there is probably no sharp dividing line between "X" structure and bainite. In the carburized specimen, Fig. 10B, the transition toward a typical high carbon bainite has been more gradual, but the structure is definitely more acicular and less open than that formed at 800 degrees Fahr. (425 degrees Cent.).

[2]E. S. Davenport, "Isothermal Transformation in Steels", TRANSACTIONS, American Society for Metals, Vol. 27, 1939, p. 837-886.

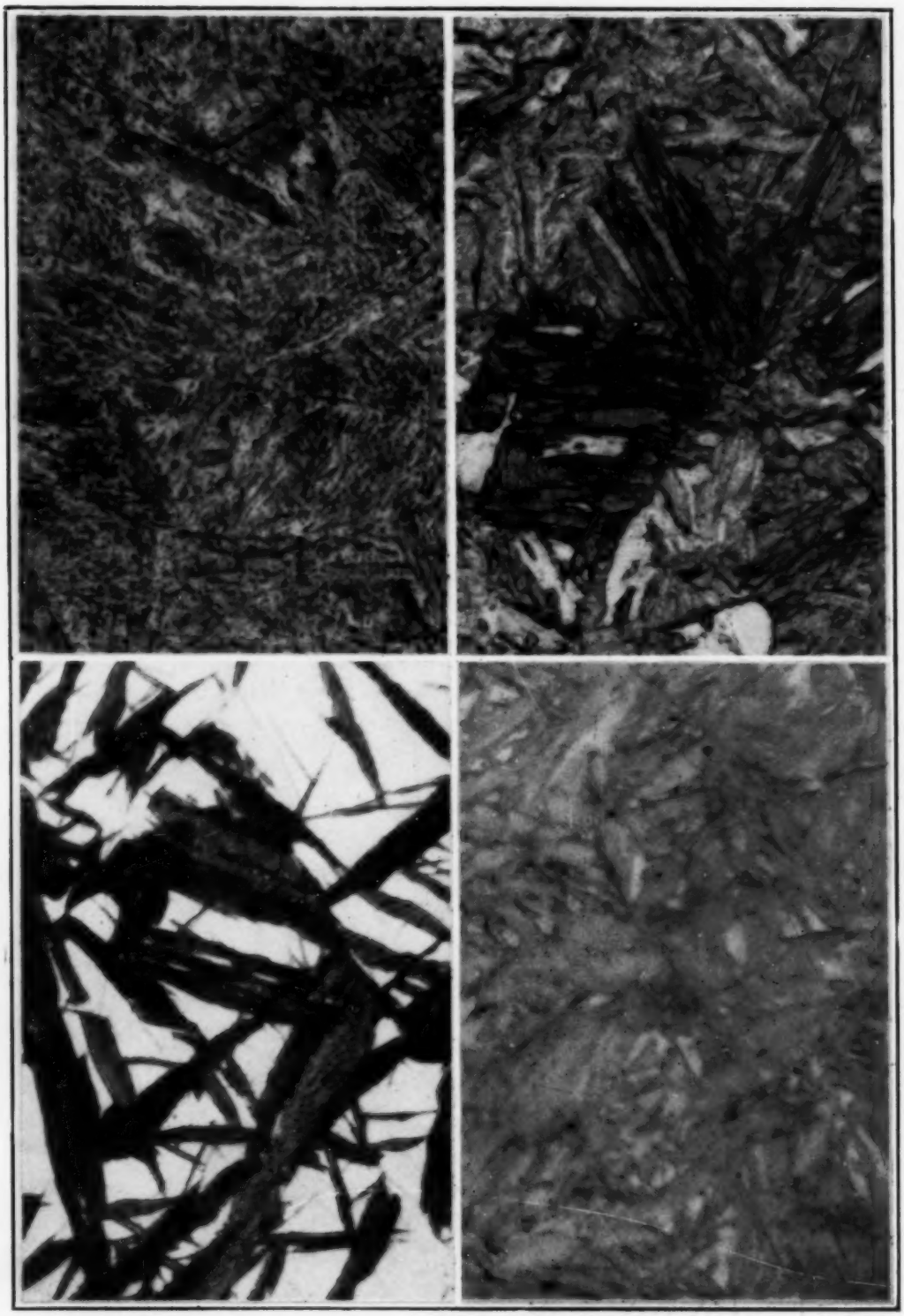

Fig. 11A—Upper.
Fig. 11B—Lower.

Fig. 12A—Upper.
Fig. 12B—Lower.

**Figs. 11 and 12—Effect of Carburization on the Structure of S.A.E. 4815. (A) Uncarburized. (B) Carburized. Fig. 11—Partial Isothermal Transformation at 500 Degrees Fahr. Fig. 12—As Quenched in Brine from 1800 Degrees Fahr. All Specimens 4 Per Cent Picral Etched. × 2000.**

The structure obtained at 500 degrees Fahr. (260 degrees Cent.) in the uncarburized specimen, Fig. 11A, differs from all the others, in that it is not a product of the direct transformation of austenite, but rather a tempered structure, because 500 degrees Fahr. (260 degrees Cent.) is below the martensite point for this uncarburized steel. On the other hand, the 500 degrees Fahr. (260 degrees Cent.) structure in the carburized specimen, Fig. 11B, is a typical low-temperature, high-carbon bainite, for this temperature is well above the martensite point of the carburized case.

Figs. 12A and 12B show respectively the martensitic structure resulting from quenching the uncarburized and carburized steels from the austenitizing temperature, 1800 degrees Fahr. (980 degrees Cent.). They are typical low and high carbon martensites, the latter showing the presence of some retained austenite.

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## DISCUSSION

**Written Discussion:** By Arthur E. Focke, research metallurgist, Diamond Chain and Manufacturing Co., Indianapolis, Ind.

Before starting my written discussion, I wish to compliment Mr. Vilella on the excellence of his photomicrographs. As reproduced on the screen, they are nothing short of beautiful.

It all seems very simple when one reads Mr. Vilella's book but it has been my experience that even with his detailed instructions, we do not obtain results such as he has shown us here today.

We are interested in this paper because we have attempted to use the information developed by isothermal transformations of case carburized parts in the solution of a practical problem, but so far our efforts have not been successful.

Briefly, we are interested, frequently, in knowing whether the physical characteristics of our carburized parts, if they are unusual in any way, have been affected by variations in the case carbon content. Quite often the parts are so small or irregular in shape that the ordinary methods of analysis for carbon cannot be applied.

On the plain carbon steels it is practical to reheat and cool slowly and to estimate the carbon content of the case by the amount of excess carbides or ferrite present, but on the alloy steels with rates of cooling fast enough to prevent carbon diffusion, the carbon divorcement in the case is not sufficient to permit any estimates of carbon content to be made.

We have made several efforts to use isothermal transformations to develop structures from which the carbon content could be estimated. The last attempt was on N.E. 8620 in which, after a preliminary survey, we standardized on a transformation temperature of 575 degrees Fahr. (300 degrees Cent.) and attempted to base our carbon estimates on the amounts of untransformed aus-

tenite after 10, 20, 30 minutes and 1 hour at this temperature. We obtained a rough correlation on samples large enough so that we could check the structures against the carbon content obtained by the usual analysis but when we attempted to apply this isothermal method we obtained so many inconsistent results that we were forced to abandon this approach to the problem.

Part of our difficulty lay in the fact that, even when making the initial correlation, although we knew from our chemical analysis that we had a rather steep carbon gradient, the variations in structure after isothermal transformation throughout the whole case would be relatively small.

Specifically, then, we would like to ask the authors whether or not they observed a similar effect in the transition zones on their samples. Also, it would appear from their data that the greatest difference between the structure in case and core could be obtained at transformation temperatures in the range just above the nose of the curve (approximately 1000 degrees Fahr.) and we wonder whether during this investigation they made any study of the transition zone which would indicate that a better correlation between carbon content and structure could be obtained if the transformations were carried out in this range.

In conclusion, then, we feel that this extension of the study of isothermal transformation structures into the field of carburized steels is a very valuable contribution and we will look forward to similar studies on some of the other grades.

### Oral Discussion

H. E. HOSTETTER:[3] Mr. Vilella has given us a concise summary of a very fine piece of work, and one which is certainly a welcome contribution to the S-curve literature. I should like to propose a little more detailed explanation for the failure of the ending curves for pearlite formation to coincide between 1100 degrees Fahr. (595 degrees Cent.) and the $Ae_1$. I wonder whether we could have Fig. 3 of the paper back on the screen? As we know, the formation of pearlite will proceed by a process of nucleation predominantly at the grain boundaries of the austenite and growth into the austenite grains. Now, as the authors have pointed out, the volume of austenite remaining after the separation of the proeutectoid constituents is greater in the carburized steel. Actually, this means that the remnants of the original austenite grains are larger in the carburized steel. They also are larger because the original austenite grain size is larger. Hence, with transformation nucleated predominantly at the grain boundaries, transformation will require a longer time for the larger remnants.

As an additional factor there might perhaps be mentioned a lower rate of nucleation which would be favored by the higher austenitizing temperature for the carburized steel, for, as Mehl pointed out in his Campbell Memorial Lecture, a higher austenitizing temperature is accompanied by a lower rate of nucleation per unit of grain boundary area. This probably was of minor significance, as is pointed out in the paper. A difference in austenitizing temperatures was not accompanied by any appreciable change in the determinations made of curves for the uncarburized steel.

[3]Metallurgical engineer, Climax Molybdenum Company, St. Louis, Mo.

**Author's Reply**

My reply to the written discussion by Mr. Focke is divided into three parts: first, photomicrographs; second, "double-crossing," and third, the martensite point.

Concerning the photomicrographs, I wish to thank Mr. Focke for his compliment and at the same time clarify a rather prevalent misunderstanding. I generally receive full credit for all the photomicrographs made at the United States Steel Corporation Research Laboratory and while this is very gratifying, it is undeserved. The fact is that these days I make but a few photomicrographs; the vast majority of them are made either by the author of the paper or by his assistant. For example, all the photomicrographs illustrating this paper were made by Mr. Cruciger, who is a young metallurgist at present serving his country in the Navy. I did establish the method, set the standard, and generally pass upon all photomicrographs released for publication, but as a rule the actual polishing, etching and photomicrography is done by the younger members of our staff.

Now coming to the point of "double-crossing," I am sorry I anticipated Mr. Focke's discussion, but the only reason why I did it was because none of the members who submitted written discussions to the previous papers was present and I, very unfortunately, assumed that Mr. Focke was also absent. Since the questions he raised were of particular interest, and since the time for presentation and discussion is rather short, I decided to touch upon his questions briefly in case I did not have time to discuss them now.

In answer to Mr. Focke's question, we did not observe any structure that could be used dependably for the estimation of carbon in case-carburized specimens. As a matter of fact, we did not examine our specimens with that purpose in mind, but we agree with Mr. Focke, that in alloy steels it is not easy, as in carbon steels, to estimate the carbon content with any degree of accuracy by merely observing the amount of proeutectoid carbide or ferrite present in slowly cooled specimens. However, such estimation can be made by utilizing the fact that the martensite point is higher the lower the carbon content of the steel. This relationship was first observed by Carpenter and Robertson in England and later Greninger and Troiano and others. To carry out this method it is necessary to work out a curve showing how the martensite point varies with carbon content in the particular steel in question. Comparison of the martensite point of the unknown specimens with this curve will tell, with considerable accuracy, the carbon content of the unknown specimen.

Referring to Mr. Hostetter's discussion, I agree with him that the difference in grain size between the carburized and uncarburized specimen, though slight, is also a reason why the ending curves for pearlite formation do not coincide between 1100 degrees Fahr. (595 degrees Cent.) and the $Ae_1$. I also agree that the fact that a higher austenitizing temperature which was used in working out the curve for the carburized steel probably influenced the rate of nucleation, as Mehl pointed out in his Campbell Memorial Lecture.

# ORDER HARDENING: ITS MECHANISM AND RECOGNITION

By David Harker

*Abstract*

*The reaction disorder to order can lead to age hardening if the structural unit of the ordered material differs in shape from that of the disordered. The gold-copper alloys near the composition AuCu furnish an example of this effect. A mechanism of hardening is postulated for these alloys, which is shown to agree with hardness, metallographic, and X-ray diffraction data.*

GOLD-COPPER alloys near the composition AuCu are well known to age harden,[1] and, since the only reactions that are known to occur in the gold-copper system are of the kind called "order-disorder transformations", the mechanism of hardening is probably connected with these reactions.

The first question that arises is whether or not an order-disorder reaction is a phase change, in the usual sense. This question was answered by preparing X-ray diffraction patterns of a 60 atom per cent gold in copper alloy which had been quenched from above its transition temperature and then aged various lengths of time at a lower temperature. These diffraction patterns are shown in Fig. 1. It is evident from these patterns that the crystal structure of the alloy changes gradually as time proceeds; the lines of the initial pattern change intensity, become diffuse, split into other lines, and, finally, the new lines move into constant positions and become sharp.

This is not the kind of sequence of patterns produced during a phase change. Such sequences have appeared in the literature and have these general characteristics: the lines on the initial pattern remain almost unaltered in position and sharpness, but decrease in intensity during the reaction, while new lines appear and increase in

[1] R. F. Vines and E. M. Wise, "Age Hardening of Precious Metal Alloys," Age Hardening of Metals, published by American Society for Metals, 1940.
This article contains an extensive bibliography in which references to most of the literature on the age hardening of gold-copper alloys can be found. For this reason no extensive bibliography is given in this paper.

A paper presented before the Twenty-fifth Annual Convention of the Society, held in Chicago, October 18 to 22, 1943. The author, David Harker, is associated with the Research Laboratory, General Electric Co., Schenectady, N. Y. Manuscript received July 8, 1943.

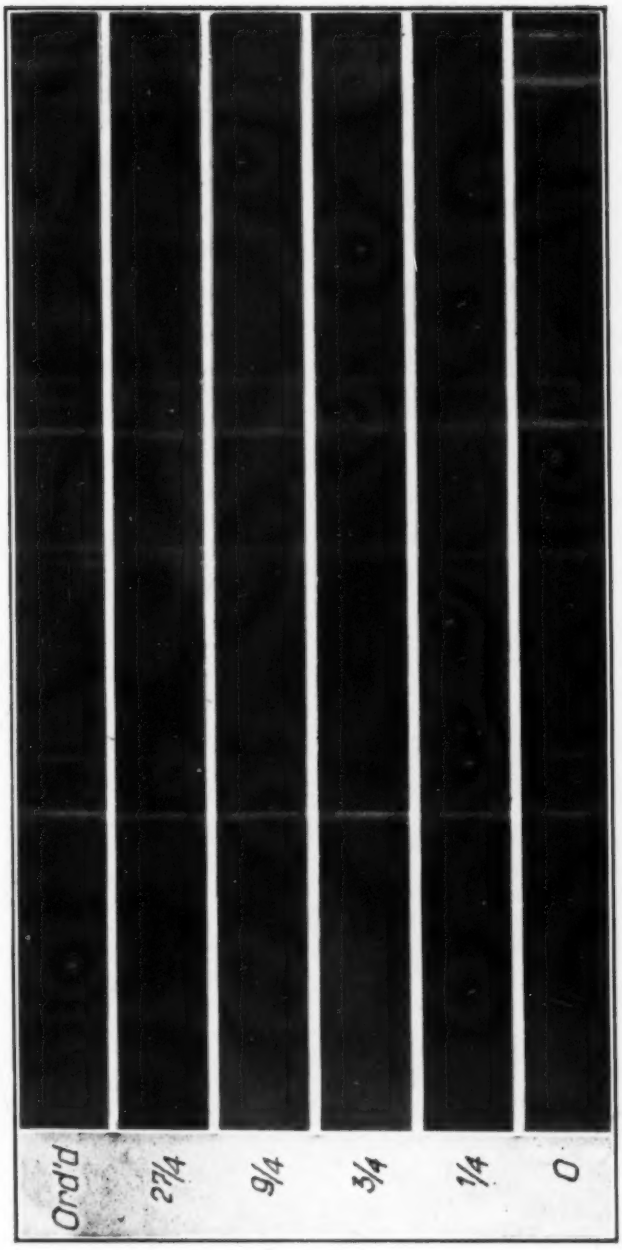


Fig. 1—X-Ray Diffraction Patterns of 60 Atom Per Cent Gold in Copper. Numbers Give Time in Hours at 260 Degrees Cent. After Quenching from 500 Degrees Cent.

intensity without much change in sharpness or position. The transformation in the 60 atom per cent gold in copper alloy is, consequently, not of the kind generally called a phase change.

It is now necessary to state more precisely what is meant by the terms "phase change" and "order-disorder reaction". These statements will have to be made in such a way that they will not only agree with the diffraction patterns, but also will be generally useful. In order to arrive at definitions which will correspond with the facts,

it is necessary to discuss in detail what the facts are. This discussion follows.

Gold-copper alloys near the composition 50 atom per cent gold can exist in two atomic arrangements. A cubic close packing of atoms, without regard to whether they are gold or copper, exists at equilibrium above about 400 degrees Cent., while at lower temperatures the equilibrium structure is tetragonal, the atomic planes parallel to one of the (002) faces of the originally cubic structure being composed alternately all of gold or all of copper atoms. These two structures frequently are called the disordered and ordered states of the alloy, respectively, because in the first only the atomic positions can be stated, but not the kind of atom in each position, while in the second the kind of atom in each position is known.

These two structures can be described analytically as follows:

*Disordered Structure*

face-centered cubic lattice.
atomic coordinates — 000, $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$;
2 gold and 2 copper atoms distributed at random among these positions.
length of edge of unit cell = $a_0$;
volume of cell = $a_0^3$.

*Ordered Structure*

base-centered tetragonal lattice.
atomic coordinates — 2Au in 000, $\frac{1}{2}\frac{1}{2}0$; 2Cu in $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$;
length of $c$-axis of unit cell = $c'_0$
length of $a$-axis of unit cell = $a'_0$
volume of cell = $a'^2_0 c'_0 = a'^3_0 \left(\frac{c'}{a'}\right)$,

where $\left(\frac{c'}{a'}\right)$ is the axial ratio.

The axial lengths of the ordered structure are different from those of the disordered structure. This difference in axial lengths will now be calculated. The volume per atom is about the same in the two structures, so that we can equate the volumes of the two unit cells:

$$a'^3_0 \left(\frac{c'}{a'}\right) = a_0^3 \qquad \text{or} \qquad a'_0 = a_0 \Big/ \left(\frac{c'}{a'}\right)^{1/3}$$

and since

$$c'_0 = a'_0 \left(\frac{c'}{a'}\right), \; c'_0 = a_0 \left(\frac{c'}{a'}\right)^{2/3}.$$

If one third the difference between $\left(\frac{c'}{a'}\right)$ and unity is called

$\delta$ so that

$$\left(\frac{c'}{a'}\right) = 1 - 3\delta$$

and if $\delta$ is rather small, then

$$a'_o = a_o\,(1 + \delta) \quad \text{and} \quad c'_o = a_o\,(1 - 2\delta)$$

to a good approximation. In the case at hand $\left(\frac{c'}{a'}\right) = 0.925$, so that $\delta = 0.025$ and the error of the approximation is of the order of $\delta^2 = 0.000625$ or about one-tenth of 1 per cent. This accuracy is sufficient for the present purposes.

This calculation shows that the unit cell of the ordered structure is 5 per cent shorter in one axial direction and 2.5 per cent longer in the two other axial directions than the disordered structure. Thus, the unit cells of the two structures have quite appreciably different shapes and corresponding interplanar distances are not the same.

When a gold-copper alloy whose composition is close to 50 atomic per cent gold is quenched from temperatures above about 400 degrees Cent. (750 degrees Fahr.) it has the disordered, cubic structure. If this quenched alloy is held for a few hours at some elevated temperature below about 400 degrees Cent. (750 degrees Fahr.), say 300 degrees Cent. (570 degrees Fahr.), it is found to have the ordered, tetragonal structure. The mechanism of this change is of considerable interest, since it is not possible for the structure to change from cubic to tetragonal without producing strains. The tetragonal phase might be produced by a process of nucleation and growth, such as occurs during the formation of copper-palladium, with the caesium chloride structure, from the cubic close-packed solid solution of that composition. This latter reaction is unquestionably a phase change in the generally accepted sense, while the ordering of $AuCu_3$, or of beta brass, is not. Indeed, this study of the change in structure of AuCu during aging was undertaken as much for the purpose of sharpening the definitions of phase change and order-disorder reaction as for its own interest.

The concepts of phase change and ordering mentioned in the last paragraph are worth a little more discussion. Perhaps the best way to present what is meant is to discuss in detail the two examples already cited.

As an example of a phase change, consider the alloy of about

50 atom per cent copper in palladium.[2] At high temperatures the structure is cubic close-packed with a random distribution of copper and palladium atoms among the occupied sites. At lower temperatures the cesium chloride type structure is stable. This is an ordered structure based on the body-centered cubic lattice in which all the atoms of one kind are at the cube corners while all the other atoms are at the cube centers. A single crystal of the cubic close-packed solid solution transforms into a polycrystalline region of the ordered body-centered cubic structure as the temperature is lowered. It takes some time for all the material to transform, as is shown by the fact that the reflections of both structures occur on the diffraction patterns of some specimens. However, the same evidence shows that there is no transition state—the material has either one structure or the other. During the transformation, therefore, the specimen must contain regions of untransformed material and of transformed material separated by sharp[3] boundaries which move as the transformed material grows at the expense of the untransformed. Thus the material at a point in the specimen changes structure suddenly as the boundary between the two phases moves across it. The process involved is one of nucleation and growth, and the rate of the transformation reaction is determined by the rate of formation of nuclei of the transformed material and by the rate of motion of its boundaries.

A slight complication can be added to the mechanism of transformation just described, if the transformed material has a different composition from the untransformed, for then the rate of motion of the boundaries is further conditioned by the rates of diffusion processes in the two phases. However, the process still remains one of nucleation and growth, which is the important point in this discussion.

On the basis of what has just been said, the following definition of a phase change is set up and will be used throughout this paper.

> A phase change is a process whereby regions with one structure nucleate and grow at the expense of regions with another structure in such a way that the two kinds of regions are sep-

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[2]At exactly 50 atom per cent copper the transformation does not occur, but it does at 49.8 atom per cent, according to the references in the Strukturbericht, Vol. 1, Ergänzungsband, *Zeit. für Krist.*, 1931.

[3]The boundary between two regions in a specimen can be called "sharp" if the shortest distance from a point definitely in one region to a point definitely in the other is of the order of magnitude of the radius of influence of an atom in the structure. This is usually not greater than three or four atom diameters. Thus, the transition between two regions with different structures is sharp if the change in structure takes place over a distance not greater than three or four atom diameters.

arated from one another by sharp boundaries at all times during the change.

Now consider the transformation from disorder to order. An example of this is furnished by the behavior of the alloy of 25 atom per cent gold in copper. At high temperatures the random cubic close-packed structure is stable; at low temperatures the atomic positions are the same, but the gold atoms are all at the cube corners while the cube face centers are all occupied by copper atoms. No appreciable change in dimensions or shape of the structural unit occurs during the transformation. It is probable that the ordering starts at nuclei—or, at any rate, that the ordering will be more nearly perfect at some places than at others in the early stages of the transformation—and that the neighborhood of a region of highly ordered material will be more likely to be somewhat ordered, so that the ordered structure dies off gradually into the surrounding disordered regions. In any event, it seems improbable that sharp boundaries should exist between ordered and disordered regions of a single crystal during the transformation, since all intermediate states of order are possible without necessitating a change in the shape of a region. During the transformation from disorder to order it seems likely that each point in the original material passes in time through increasing states of order, and that highly ordered regions are separated from regions of disorder by broad bands of material in which the state of order changes gradually with position—except, perhaps, at grain boundaries.

At compositions different from those which form the most highly ordered structures the ordering reaction seems to proceed to the greatest order possible without causing the specimen to separate into regions with different compositions.

The discussion above makes possible a definition that will be used throughout this paper:

> An order-disorder transformation is a process whereby one structure changes to another without the presence of sharp boundaries anywhere[4] in the system at any time.

The acceptance of the definitions of phase change and order-disorder reaction that have just been expressed carries with it several consequences. For instance, since an order-disorder transformation takes place without the formation of sharp boundaries, no phase

[4]At grain boundaries there may be a sharp transition from ordered material in one grain to disordered in another. The definition refers to the state of affairs within a region that was a single grain at the beginning of the ordering process.

change has occurred and both the ordered and disordered states of the system belong to the same phase. This corollary of the definitions makes it unnecessary to draw lines on phase-rule diagrams which separate fields of order and disorder. This is realistic, since order-disorder transformations do not follow the laws of phase changes.

Another corollary follows which is rather disconcerting: the fact that two substances of the same composition have different structures does not mean that two different phases necessarily exist at that composition. It is consequently possible to question the existence of many of the phase changes reported in the literature. It will be necessary to establish the mechanism of transformation between structures before they can be said to belong to different phases.[5]

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[5]Whether or not two homogeneous specimens of material, A and B, are considered as different phases is sometimes largely a matter of convenience. If the usual way to make B from A involves the presence in the system, at some stage of the process, of sharp boundaries between regions with different properties, it is only common sense to call them different phases. If, on the other hand, the most convenient processes for changing A to B involve no sharp boundaries, it is normal to say that A and B are the same phase. Sometimes it is about as easy to go from A to B by means of a phase change as without one, and then it is hard to tell whether they should be called different phases or not.

The liquid zinc-bismuth alloys furnish a good example for discussion. Above about 820 degrees Cent. (1510 degrees Fahr.) the two liquid metals are mutually soluble in all proportions, but as the temperature is lowered a solubility gap appears. At 650 degrees Cent. (1200 degrees Fahr.) the two liquid layers contain, respectively, about 25 and 85 per cent zinc. Suppose it were required to make a liquid alloy of 20 per cent zinc from one of 90 per cent zinc at 650 degrees Cent. (1200 degrees Fahr.). As liquid bismuth at 650 degrees Cent. (1200 degrees Fahr.) is added to liquid 90 per cent zinc in bismuth with stirring, droplets of liquid 25 per cent zinc in bismuth will soon appear, and continue to increase in size and number until they coalesce and surround the initial phase. As more bismuth is added, the remaining droplets of the initial phase disappear and finally only one phase will be present. This process has involved a phase change.

The process might have been carried out in another way, however. The 90 per cent zinc in bismuth could have been heated to 850 degrees Cent. (1560 degrees Fahr.) and the liquid bismuth added at this temperature until the alloy contained only 20 per cent zinc. The temperature could then have been lowered to 650 degrees Cent. (1200 degrees Fahr.). This process would have involved no separation into two phases, so that no phase change would have occurred.

The question whether or not the two liquid alloys, 90 per cent zinc in bismuth and 20 per cent zinc in bismuth at 650 degrees Cent. (1200 degrees Fahr.), are different phases can only be answered if the process by which one is produced from the other is known. If the process at constant temperature is used, they would be considered different phases—if the heating process is used, they would be called the same phase. In many cases there is no absolute criterion to apply in deciding whether or not two alloys belong to the same phase, and the question only has meaning in terms of the process used in passing from one to the other.

The 50 atom per cent gold-copper alloy already mentioned provides a case in point. As noted previously, there is considerable change in structure during the transition from the cubic to the tetragonal state. The question of the mechanism of this change can now be phrased thus: Is it a phase change or an ordering reaction? Since there is a considerable change in the shape of the unit cell, the start of the transformation somewhere within a single crystal of the face-centered cubic solid solution must set up stresses. These stresses might be expected to lead to a shearing away of the transformed material from the untransformed, thus providing the sharp boundaries characteristic of a phase change. However, if this shearing away does not take place, the process might well be classified as an order-disorder change.

It is known that no pronounced hardening occurs on ordering, if the ordered and disordered structures possess a common unit cell size and shape, but an ordering involving the production of stresses, and their concomitant strains, might well result in the hardening observed in slowly cooled copper-gold alloys. A series of experiments was performed in order to investigate this question.

"Fine" gold (from Handy and Harman) and OFHC copper were melted in graphite crucibles in a hydrogen furnace. When melted, the liquid was stirred with a graphite rod. The furnace temperature was then lowered very slowly through the melting range of the alloy to about 450 degrees Cent. (840 degrees Fahr.), the crucible and contents were removed from the furnace, and the ingot of alloy quenched in water. The ingot was then pressed to break up the cast structure and rolled to 0.050-inch thick sheet. Filings were taken from a sheared edge of the sheet for X-ray examination and the rest of the sheet was cut into pieces 0.5 by 0.75 inch for microscopic examination. A set of specimens was made in this way of each of three alloys: 60, 50, and 40 atom per cent gold in copper, respectively. All the specimens, sheet and filings, were heated for 2 hours at 500 degrees Cent. (930 degrees Fahr.) and quenched in water. These specimens gave X-ray diffraction patterns typical of the face-centered cubic lattice, and polished and etched surfaces showed under the microscope the familiar, highly twinned, smooth grains of recrystallized face-centered cubic metals.

Two sheet specimens and some filings were subjected to the following treatments:

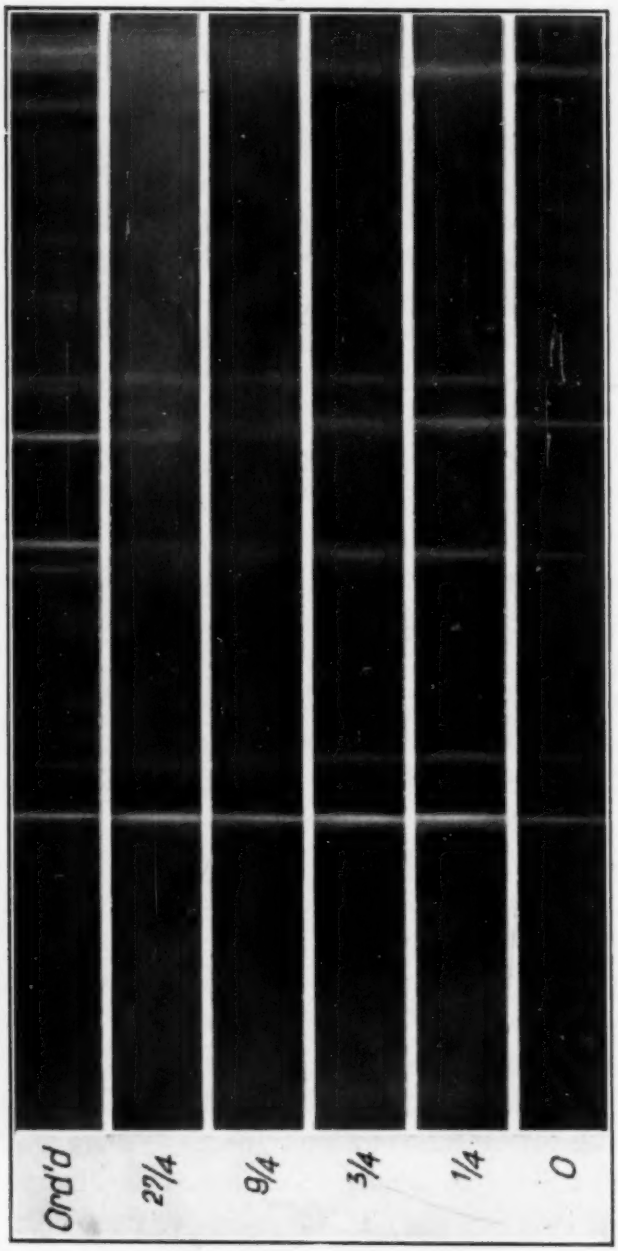


Fig. 2—X-Ray Diffraction Patterns of 50 Atom Per Cent Gold in Copper. The Numbers Give the Time in Hours at 218 Degrees Cent. After Quenching from 500 Degrees Cent.

All compositions; 180 degrees Cent. for 1/4, 3/4, 9/4, and 27/4 hours,
All compositions; 220 degrees Cent. for 1/4, 3/4, 9/4, and 27/4 hours,
60 and 40 gold; 260 degrees Cent. for 1/4, 3/4, 9/4, and 27/4 hours,
50 gold; 300 degrees Cent. for 1 hour.
60 and 40 gold; 300 degrees Cent. for 27/4 hours.

In all there are 38 treatments.

One of the sheet specimens was used to find the hardness on the Rockwell "G" scale ($\frac{1}{16}$-inch steel ball, 150-kilogram load); the other was used for microscopic examination, and the filings were used in

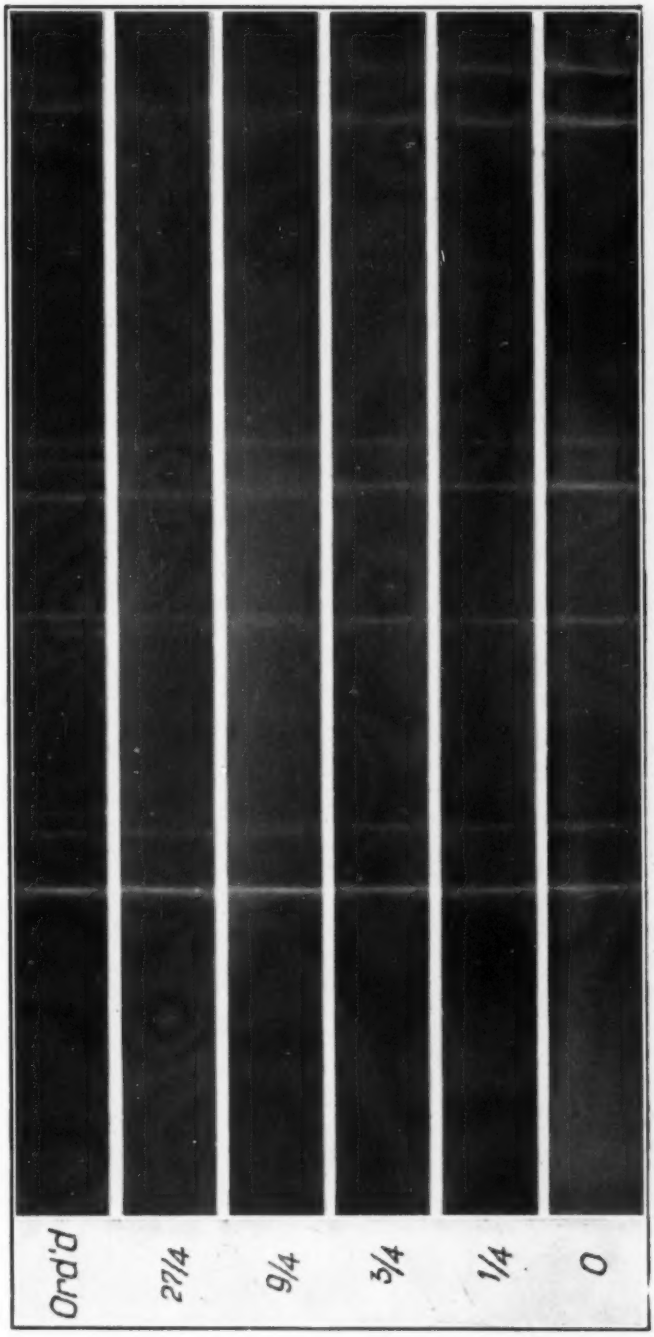


Fig. 3—X-Ray Diffraction Patterns of 40 Atom Per Cent Gold in Copper. The Numbers Give the Time in Hours at 260 Degrees Cent. After Quenching from 500 Degrees Cent.

preparing X-ray diffraction patterns.[6]

[6]The hardness was taken to be the average of ten readings from one side of the 0.5 by 0.75 by 0.050-inch piece. There was no change in the appearance of the other side of the piece in any case.

The etch used to bring up the structure was a mixture of hydrochloric acid and chromium trioxide.

The X-ray patterns were made in a cylindrical camera 57.3 millimeter in radius, using a 0.020-inch slit system and Cu $K\alpha$ radiation filtered through 0.001 inch of nickel.

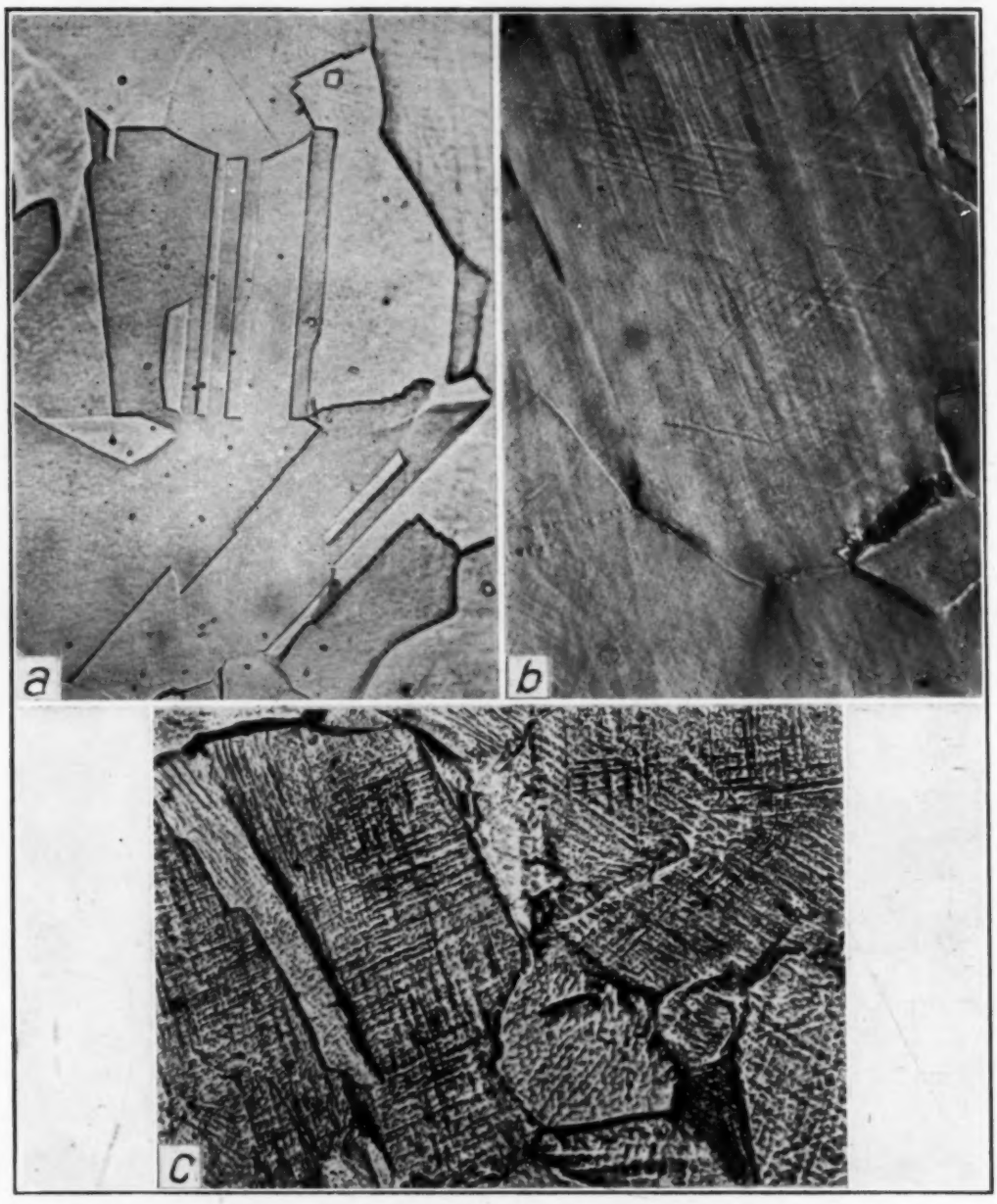


Fig. 4—Photomicrographs of 50 Gold-50 Copper Alloy (Atom Per Cent). × 500. (a) 2 Hours at 500 Degrees Cent., Quenched. (b) 2 Hours at 500 Degrees Cent., Quenched. 2 Hours, 15 Minutes at 217 Degrees Cent., Quenched. (c) 2 Hours at 500 Degrees Cent., Quenched. 6 Hours, 45 Minutes at 217 Degres Cent., Quenched.

In general the hardness increased during the final heat treatment, and the increase in hardness ran parallel with changes in the microstructure and X-ray diffraction pattern.

The microstructure of the quenched specimens was very similar to that of copper which has been annealed after cold working; the grains were highly twinned with smooth structureless surfaces be-

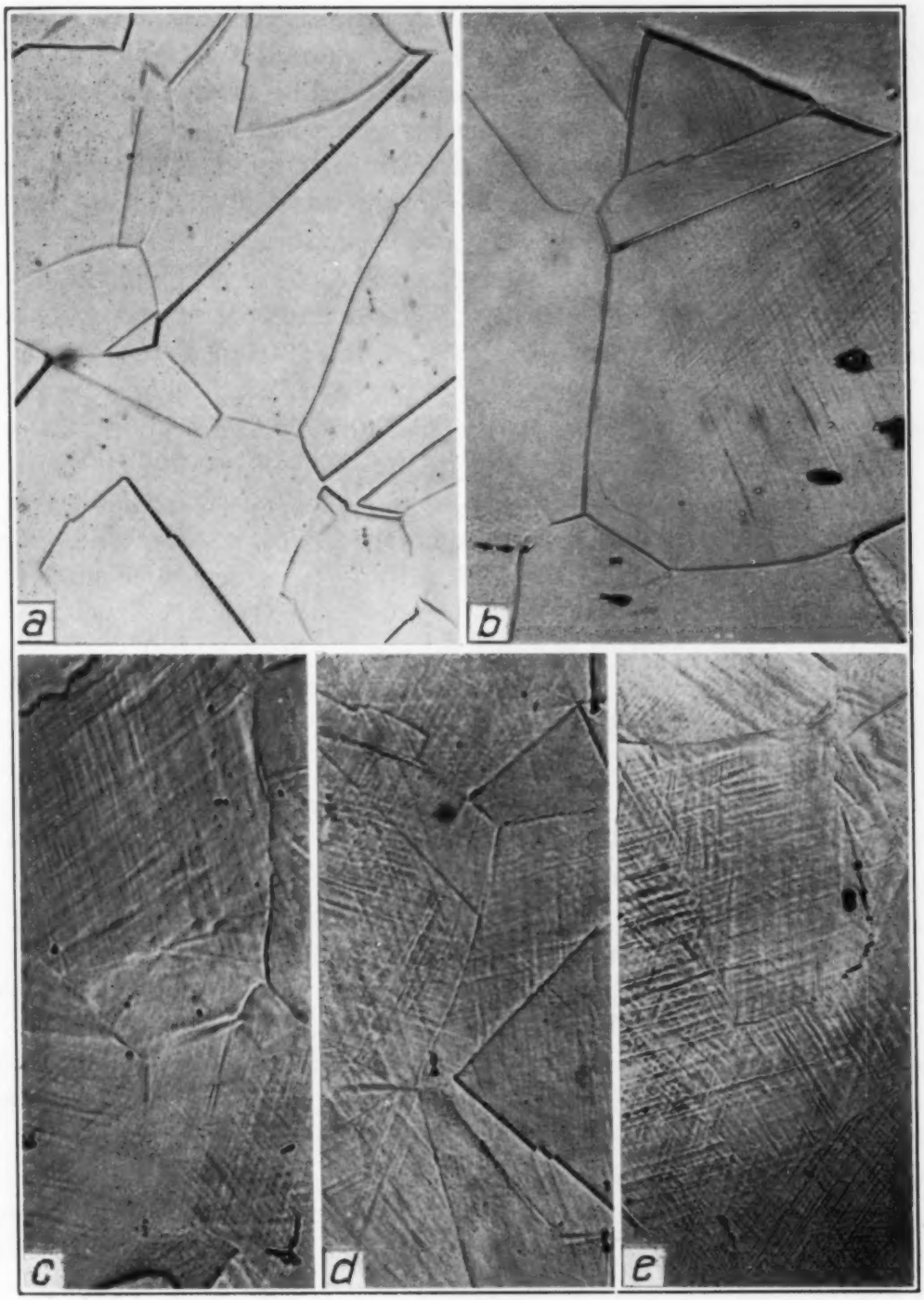


Fig. 5—Photomicrographs of 60 Gold-40 Copper Alloy (Atom Per Cent). × 500. (a) 2 Hours at 500 Degrees Cent., Quenched. (b) 2 Hours at 500 Degrees Cent., Quenched. 15 Minutes at 260 Degrees Cent., Quenched. (c) 2 Hours at 500 Degrees Cent., Quenched. 45 Minutes at 260 Degrees Cent., Quenched. (d) 2 Hours at 500 Degrees Cent., Quenched. 2 Hours, 15 Minutes at 260 Degrees Cent., Quenched. (e) 2 Hours at 500 Degrees Cent., Quenched. 6 Hours, 45 Minutes at 260 Degrees Cent., Quenched.

tween the twin planes and grain boundaries. As the time of heating increased the previously smooth surfaces developed rippled regions in which the ripples ran straight and parallel or made definite angles with one another. These rippled regions increased in size and definition as the heating continued, until in some cases, they covered all the grains. Figs. 4 and 5 show prints of photomicrographs illustrating this progressive change in structure.

The X-ray diffraction patterns also showed a change in character as the time of heating increased. The quenched specimens always showed only the sequence of lines expected from a face-centered lattice (with lattice constants varying with the composition, of course). The first change in the specimen during heating was reflected in a pronounced decrease in the intensity of the (004) line relative to the (222) line. About the time that the (004) line became almost invisible on the pattern, the other lines, except (111) and (222), began to broaden. This broadening then continued until the lines split into the components required by a tetragonal structure of the AuCu type. Finally, the lines of the AuCu type structure sharpened up and the lines of mixed indices (h, k and l not all odd or all even) began to appear at the longest times of heating at the highest temperatures. Figs. 1, 2, and 3 show reproductions of X-ray diffraction patterns illustrating the sequence of changes just described. It is to be noted that a phase change would give a different sequence of diffraction patterns: the lines of the original phase would decrease in intensity (and perhaps shift position slightly) while the lines of the new phase would appear and then increase in intensity. The diffraction patterns obtained in this work indicate a quite different mechanism of transformation.

A theory has been constructed which accounts for the X-ray diffraction effects, and is in harmony with the microstructure and hardness changes; it will be developed in the following paragraphs. One of the results of the point of view to be taken is a set of criteria for determining whether or not a transformation is a phase change or an ordering process, as it will be shown that the diffraction effects observed could be produced by an ordering process, as defined above.

## Theory of the Ordering Process in AuCu

A troublesome point in the change from the cubic structure of the disordered solid solution to the tetragonal structure of the ordered

state of alloys near the composition AuCu has been the distortion necessary to produce a small region of the ordered structure in a large region of the disordered structure. Imagine a large region of the disordered structure in the middle of which a small region of the ordered structure has formed. Such a situation might be symbolized by a diagram like Fig. 6. The small ordered region creates a tension in the neighboring disordered material where its boundary

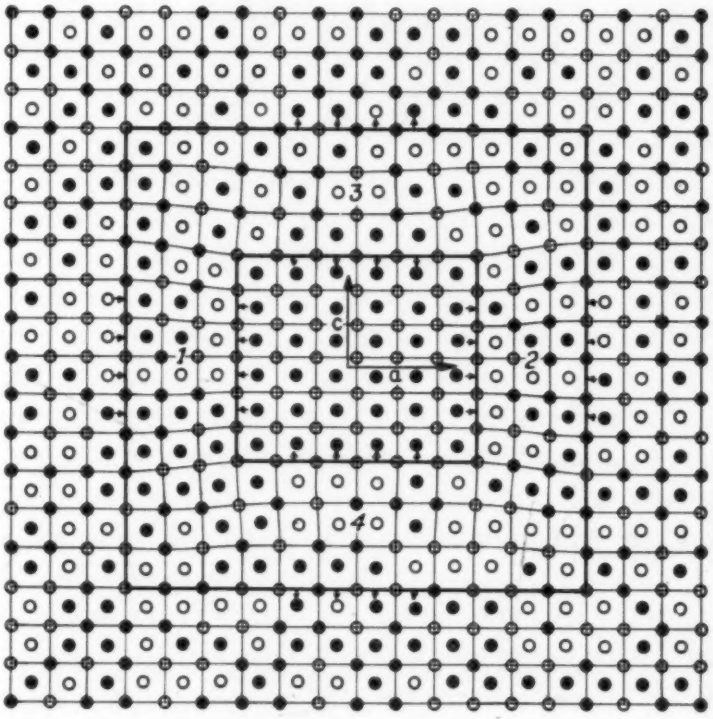


Fig. 6

is about parallel to the gold and copper layers, and a compression in the direction at right angles to the tension. One might say, using crystallographic terms, that there is a tension in the direction of the *c*-axis of the ordered region and a compression in the perpendicular directions. Thus there is compression in regions 1 and 2 of Fig. 6 and tension in regions 3 and 4. If the temperature is below that of the order-disorder transition, the ordered region will increase in size by accretion from the neighboring disordered material, and this will increase the stresses in the system. This process will continue until the free energy of the whole system can no longer be decreased by growth of the ordered region, which will then have reached its maximum size under the assumed conditions; or else the surrounding

disordered material will deform under the stresses and the ordered region will continue to grow. In either case, the disordered material in the *c*-direction from the ordered material will be under tension in the *c*-direction and the disordered material in an *a*-direction from the ordered material will be under compression in the *a*-direction.

It will be easier for a nucleus of the tetragonal ordered structure to form with its *c*-axis in a direction in which the disordered structure is compressed or with its *a*-axis in a direction in which the disordered structure is under tension, since the formation and growth of such a nucleus will relieve the compression or tension, respectively. For the same reason it is likely that a nucleus of order will have a greater chance of forming in such a region than it would have in an unstressed region of the disordered structure. These two ideas lead to the expectation that a region of order growing from a nucleus in a large mass of disordered material is likely to induce the formation of other nuclei of order in its neighborhood with their *c*-axes pointing in the directions of *a*-axes of the original nucleus. These nuclei will grow at about the same rate as the original one, so that it will soon be surrounded and its growth stopped for lack of disordered material on which to feed. This complex arrangement of ordered regions will induce still other nuclei in its neighborhood; and the process will continue until all the disordered material is used up.

The assumptions made in the preceding paragraph are based on the idea that the ordering process will take place in such a way as to produce the minimum stress in the system. At the end of this process the shape of a block of originally disordered material would be almost unchanged. In order to accomplish this result the total length in each of the original cube edge directions must be preserved, and this can be done only by having the ordered regions so distributed and oriented that there is twice as much *a*-axis length as *c*-axis length along these directions. If the ordered regions are roughly the same size and about the same length in all three directions, their arrangement and orientation is rather limited by the requirements postulated in the foregoing discussion.

To recapitulate and make precise the assumptions brought forth in the preceding discussion:

(1) The ordered structure is tetragonal with its axial ratio, $\frac{c}{a}$, less than unity.

(2) The ordered structure has its axes in the same directions as those of the disordered structure from which it grows.

(3) The ordered structure consists of cells all about the same size and approximately equiaxed.

(4) Adjoining cells never have both their $c$-axes parallel to the line joining them.

(5) A line parallel to one of the original cube directions will cross twice as many cells with their $a$-axes in that direction as cells with their $c$-axes in that direction.

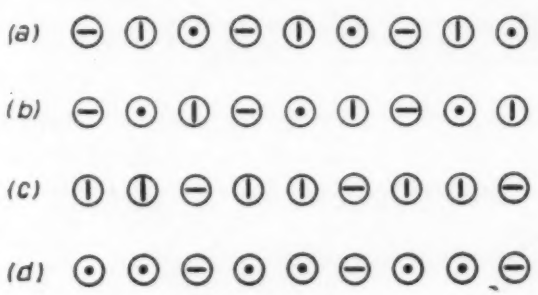


Fig. 7

(6) The cells of ordered structure are arranged in approximate simple cubic packing.

These assumptions allow a model of the cell structure of the ordered material to be constructed. Assuming the cube directions of the original disordered structure to lie along directions parallel to the edges of the page and perpendicular to the page, and denoting a cell by a circle containing a short line showing the direction of its $c$-axis, or a dot if its $c$-axis is perpendicular to the plane of the page, the sequences along an original cube direction shown in Fig. 7 are possible.[7]

The problem is to construct from rows of these kinds, simple cubic arrangements in which every row of cells along an original cube edge direction is of one of these kinds. This can be done in many ways. One of these arrangements is outstanding in that it not only preserves all the original cube lengths, but also preserves the angles between them—by cancelling the shear strains produced across the (111) planes during ordering. This structure is diagrammed in Fig. 8. The structure consists of layers parallel to one of the (111) planes, in each of which the tetragonal $c$-axis points along only one

[7]Other sequences than those shown are also possible, but they can all be built up from these. The given sequences all have a period of three. All other sequences have larger periods.

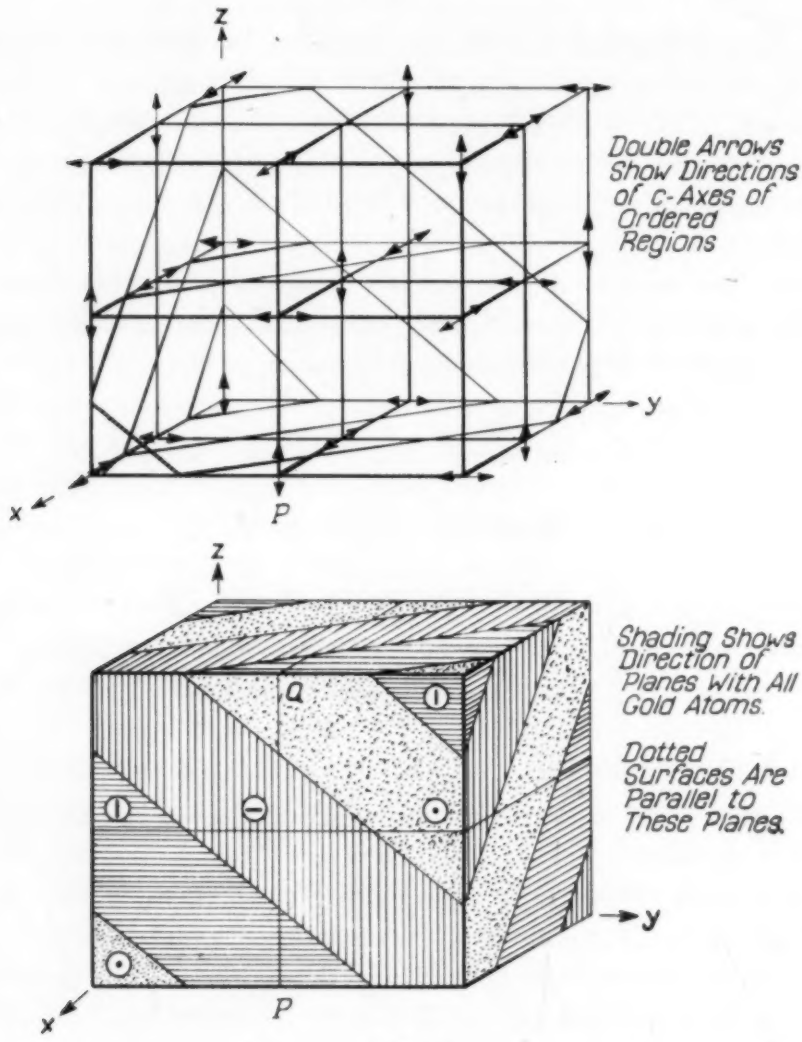


Fig. 8

of the original cube directions. Three successive layers have their *c*-axes in the three different cube directions.

The photomicrographs have an appearance in agreement with this structure. The parallel ripples on the etched surface have two, three, or four directions in any one grain, but never more than four. This suggests that they are parallel to planes of the form (111). See, for instance, Figs. 4 and 5.

It will now be possible to discuss the changes in X-ray diffraction effects which occur during the ordering reaction.

The first effect that appears as the disordered structure is aged at an elevated temperature is the decrease in intensity and eventual disappearance of the (004) reflection of the face-centered cubic type pattern. The other lines remain relatively unchanged in character.

("Relatively unchanged" includes intensity and breadth changes up to 30 per cent.) A decrease in intensity can be due only to an increase in the phase differences between the rays scattered in that direction. The origin of such phase differences is usually sought in the changed relative positions of atoms within the unit of structure, but other changes in atomic positions can accomplish the same result. In the case at hand, the *average* interplanar distance perpendicular to a cube face of the disordered structure does not change during the ordering process, but it does vary from place to place. For instance, in Fig. 8, the $d_{(002)}$ changes from the value of $c_0$ for the tetragonal ordered structure to that of $a_0$ for the same structure, as the line from P to Q is traversed. Near P the distance between successive (002) planes is smaller than the average, near Q it is greater, and somewhere in between it passes through the average—in the region between two ordered cells of different orientation.

Suppose that the (002) planes at P and Q are $na_0$ apart, where $a_0$ is the lattice constant of the disordered structure. Then the rays scattered from these planes in the proper directions for the Bragg reflections (002), (004), etc., of the disordered lattice will be exactly in phase and will reinforce each other. All the other (002) planes between P and Q will be somewhat shifted from their positions in the disordered structure, however, and rays scattered from them will be more or less out of phase with the rays from the planes at P and Q. Thus, the intensities of the Bragg reflections (002), (004), etc., will be decreased below their values for the disordered structure.

A sample calculation for an idealized case will show how this came about. Take a distance $6kd_{(002)}$ parallel to one of the cube edge directions of the disordered structure. Assume that this distance will contain 4k interplanar distances $\frac{1}{2}a'_o$ and $2k$ interplanar distances $\frac{1}{2}c'_o$ in the completely ordered structure. (The primed symbols refer to the ordered tetragonal structure.) Let $a'_o = a_0(1+\delta)$ and $c'_o = a_0(1-2\delta)$ with $\delta$ rather small. Thus, a distance $2ka'_o = 2ka_0(1+\delta)$ has the interplanar spacing $d'_{(200)} = \frac{1}{2}a'_o$, and a distance $kc'_o = ka_0(1-2\delta)$ has the interplanar spacing $d'_{(002)} = \frac{1}{2}c'_o$. Fig. 9 will make this clearer. Assume that this sequence repeats periodically. Then there are atomic planes at $0, \pm d_{(002)}(1+\delta), \ldots\ldots, \pm d_{(002)}\,2k\,(1+\delta), \pm [3kd_{(200)} - (k-1)d_{(002)}(1-2\delta)]$,

..... $\pm$ $[3kd_{(002)} - d_{(002)}\ (1\text{-}2\,\delta]$, $3kd_{(002)}$, and positions derived from these by adding integral multiples of $6kd_{(002)}$. Setting up the intensity formula and summing the series, the amplitude per plane of atoms comes out to be

$$F_h = \frac{f}{6k}\left[\frac{\sin 2\pi \frac{h}{2}\left(2k+\frac{1}{2}\right)\delta}{\sin 2\pi \frac{h}{2}\frac{1}{2}\delta} + \frac{\sin 2\pi \frac{h}{2}(2k-1)\,\delta}{\sin 2\pi \frac{h}{2}\delta}\right]$$

If $\delta = 0$, $F_h = f$, where f is the average amplitude of scattering per plane of atoms parallel to a cube face. This quantity varies with the Bragg angle $\Theta$ in a well known way. For $\delta = 0.025$ (corresponding to $\frac{c}{a} = 0.925$, the value for highly ordered AuCu) and $k = 4$, the formula becomes

$$F_h = \frac{f}{24}\left[\frac{\sin 2\pi \cdot 0.10625h}{\sin 2\pi \cdot 0.00625h} + \frac{\sin 2\pi \cdot 0.0875h}{\sin 2\pi \cdot 0.0125h}\right]$$

$$\text{If } h = 2, \quad F_h = \frac{f}{24}\left[\frac{0.972}{0.0785} + \frac{0.891}{0.156}\right] = 0.754f$$

$$\text{If } h = 4, \quad F_h = \frac{f}{24}\left[\frac{0.454}{0.156} + \frac{0.799}{0.309}\right] = 0.229f$$

The corresponding intensities are the squares of the amplitudes:

$$I_{(002)} = 0.569f^2, \quad I_{(004)} = 0.052f^2$$

The disordered structure would give $I = f^2$ for both cases.

If the structure during the early stages of ordering were exactly the idealized one assumed in the calculations, the (002) reflection should decrease 43 per cent in intensity and the (004) should decrease 95 per cent. Qualitatively, this is the sort of intensity change that actually occurs.

The actual structure, however, is certainly not as sharply defined as the one assumed. In the first place, the value of $\frac{c}{a}$ probably is much nearer unity in the early stages of ordering, since the segregation of gold and copper atoms into alternate (002) planes must be

far from complete. This means that $\delta$ is much smaller in the real case than in the ideal. Secondly, the space between two ordered regions must be occupied by quite disordered material, since two ordered regions of different orientation cannot fit together across a plane. The actual state of affairs along a cube direction of the originally disordered material is probably more like that shown in Fig. 10. Both these corrections to the assumptions of the simple theory allow a great increase in the size of the ordered regions

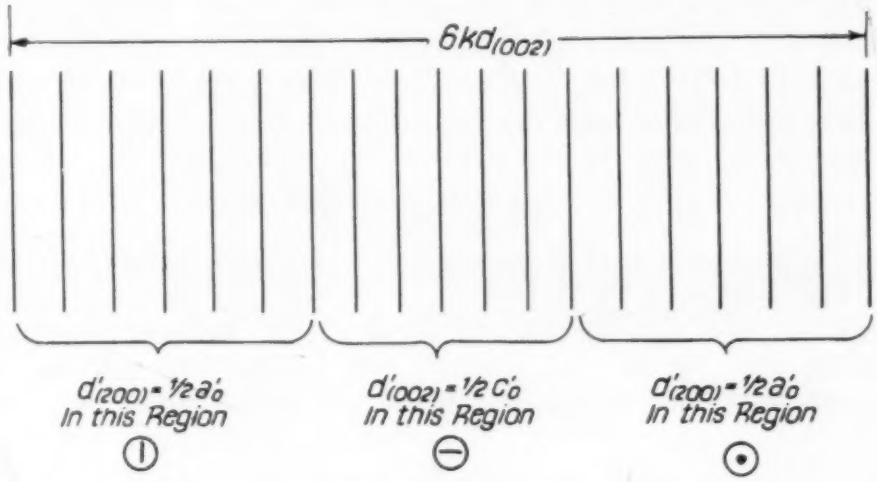


Fig. 9

before the intensities of the (002) and (004) reflections will be decreased to the values just calculated. Consequently, the nuclei of order may be quite far apart, even several hundred atom diameters, and the effects of incipient ordering on the intensities of the (002) and (004) reflections will still be of the kind just calculated.

The question now arises as to why the (004) and (400) reflections of the ordered structure do not appear as soon as tetragonal material is formed in sufficient quantity to account for the decrease in intensity of the (004) reflection belonging to the disordered structure. The reason seems to be this: the regions over which the tetragonal $a_o'$ and $c_o'$ do not change with position must be very small, so that the line breadth of these reflections must be very great. In addition, the different values of $a_o$ and $c_o$ will produce these broad reflections at various positions, and the result will be a darkening of the background over a large region near the (004) reflection of the disordered structure. There is a slight increase in the background during the early stages of ordering, but since no great precautions were taken to insure a pure background, no definite conclusions can

be drawn. As the aging time is increased, the tetragonal (004) and (400) reflections do appear—rather broad and weak, and not in their final positions. Their first appearance coincides approximately with the vanishing of the cubic (004). This means that ordering sufficient to give regions large and uniform enough to produce something approaching the X-ray diffraction effects expected from crystalline material is also enough to bring about what amounts to random phase shifts between these regions.

At the same stage of aging as that which brings about the vanishing of the cubic (004) reflection, the other reflections, except the orders of (111), begin to broaden. The question which naturally arises is this: Why have the other lines not been behaving similarly

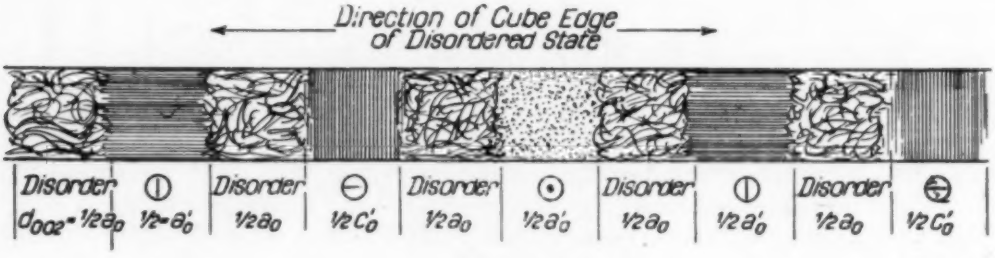


Fig. 10

to the cubic (004)? The answer can be based on the same theory as before. In the case of the cubic (004) the phase differences between rays reflected from different atomic planes became great enough to almost extinguish the corresponding reflection before the tetragonal regions were large enough to produce sharp (004) and (400) reflections. In the case of such a cubic reflection as (220), the same stage of ordering will not produce as great phase differences, and so the cubic reflection will not have completely vanished by the time the corresponding tetragonal reflections, (220) and (202), begin to appear. The resulting appearance of the reflections would be a broadening and decrease in intensity.

Fig. 2 illustrates the changes in diffraction effects occurring during the ordering reaction in 50 atom per cent gold-copper. It is seen that the order of events is essentially as described in the foregoing paragraphs.

The structural changes accompanying the aging of gold-copper alloys near the composition AuCu being known, they can now be correlated with the hardness changes which take place at the same time. In general, the greater part of the hardening takes place before

the X-ray diffraction pattern shows any great changes. Thus, the 60 atom per cent gold in copper alloy had a Rockwell "G" hardness of 31 as quenched from 500 degrees Cent. (930 degrees Fahr.), and this figure rose to 75 after the specimen was heated at 260 degrees Cent. (500 degrees Fahr.) for 15 minutes. During this time the (004) reflection had nearly vanished, but very little change had taken place in the positions and breadths of the other reflections. After the sample was heated for 6.75 hours at 260 degrees Cent. (500 degrees Fahr.) the hardness was 77, and the diffraction pattern was almost that of a completely ordered alloy. The photomicrographs of these alloys appear in Fig. 5, and show clearly that the rippled structure is already quite distinct in the 60 atom per cent gold in copper alloy after 15 minutes at 260 degrees Cent. (500 degrees Fahr.). The hardening, therefore, is connected with the early stage of ordering.

Table I presents the data on hardness, microstructure, and X-ray diffraction obtained in the course of this investigation. The columns headed "hardness" and "microstructure" are self explanatory. The column headed "X-ray diffraction pattern" contains notations on the quality of the pattern.

X-ray diffraction patterns were obtained from samples of each of the alloys after heating them at 300 degrees Cent. (570 degrees Fahr.) and for long enough times to make it probable that they were completely ordered. The 50 atom per cent gold alloy showed strong superstructure lines after 1 hour at 300 degrees Cent. (570 degrees Fahr.), but the 40 atom per cent gold alloy showed only faint superstructure lines after 6 hours, and the 60 atom per cent gold alloy showed none after 6 hours. The weakness or non-appearance of superstructure lines, even though the tetragonal structure has formed, shows that the atomic ordering process is incomplete. The atoms in the minority must be largely segregated in alternate (002) planes in the 40 and 60 atom per cent gold alloys or the structure could not reasonably be tetragonal, but the arrangement in the planes must still be quite random. It is hoped to study this question more fully at some future time.

The Rockwell "hardness" of a metal is not a simple property, being determined not only by the ease and rate of slip on glide planes of the metal's crystals, but also by the rate and amount of work hardening. Nevertheless, it is probably safe to say that the "harder" a sample of metal, the greater its resistance to slip, and conversely.

**Table I**

**Properties of Aged Gold-Copper Alloys. (All Alloys Quenched After Two Hours at 500 Degrees Cent. Before Aging)**

| Atom % gold | Aging Temp. °C. | Aging Time, Hrs. | Hardness Rockwell G | Microstructure | X-ray diffraction pattern |
|---|---|---|---|---|---|
| 60 | ... | 0 | 31 | Smooth grains | Cubic close packed |
| 60 | 181 | ¼ | 54 | | " |
| 60 | 181 | ¾ | 63 | | " |
| 60 | 181 | 2¼ | 64 | | " |
| 60 | 181 | 6¾ | 74 | | " |
| 60 | 217 | ¼ | 66 | | Cubic close packed (004) weak |
| 60 | 217 | ¾ | 68 | | " |
| 60 | 217 | 2¼ | 72 | | Cubic close packed (004) weak, and *a* doublet not resolved |
| 60 | 217 | 6¾ | 80 | | 004 absent; all lines broad except (111) and (222). |
| 60 | 260 | ¼ | 75 | Slight ripple pattern in some grains. | " |
| 60 | 260 | ¾ | 75 | Distinct ripple pattern in most grains. | (331), (420) split, tetr. (400) visible. All lines broad except (111) & (222). |
| 60 | 260 | 2¼ | 76 | Ripple pattern in all grains. | Tetr. struc., lines broad. |
| 60 | 260 | 6¾ | 77 | Heavy ripple pattern in all grains | Tetr. St., lines sharper. |
| 60 | 300 | 6 | | | Tetr. St., lines sharp. No superstructure lines. |
| 50 | ... | 0 | 83 | Slight local ripple structure in a few grains. | Cubic close packed. |
| 50 | 181 | ¼ | 83 | " | Cubic close packed. (004) not strong. |
| 50 | 181 | ¾ | 79 | " | (004) weak. |
| 50 | 181 | 2¼ | 85 | Slight ripple pattern in most grains. | (004) very weak, lines broad, except (111) and (222). |
| 50 | 181 | 6¾ | 88 | " | " |
| 50 | 217 | ¼ | 83 | Slight ripple pattern in some grains. | Cubic close packed. (004) weak, *a* doublet not resolved. |
| 50 | 217 | ¾ | 87 | Distinct ripple pattern in most grains. | Cubic close packed. (004) absent, lines very broad. |
| 50 | 217 | 2¼ | 89 | Distinct ripple pattern in all grains. | Tetr. (400) present but broad, other lines broad and weak. |
| 50 | 217 | 6¾ | 93 | Heavy ripple pattern in all grains. | Tetr. structure, lines broad, superstructure present. |
| 50 | 300 | 1 | | | Tetr. structure, lines sharp, superstructure present. |
| 40 | ... | 0 | 15 | | Cubic close packed |
| 40 | 181 | ¼ | 36 | | " |
| 40 | 181 | ¾ | 49 | | " |
| 40 | 181 | 2¼ | 49 | | " |
| 40 | 181 | 6¾ | 51 | | " |
| 40 | 217 | ¼ | 58 | | " |
| 40 | 217 | ¾ | 57 | | " |
| 40 | 217 | 2¼ | 54 | | " |
| 40 | 217 | 6¾ | 64 | | Cubic close packed, (004) weaker. |
| 40 | 260 | ¼ | 61 | | Cubic close packed, (004) weaker. |
| 40 | 260 | ¾ | 66 | | Cubic close packed, (004) very weak. |
| 40 | 260 | 2¼ | 80 | | Lines very broad, (004) extinct. |
| 40 | 260 | 6¾ | 83 | | Tetr. structure lines very broad. |
| 40 | 300 | 6 | | | Tetr. structure lines sharp. Superstructure. |

In most metals with the cubic close-packed structure slip occurs predominantly on the octahedral planes—those of the form {111}—so that four sets of parallel glide planes are available. If three of these sets of planes were keyed to prevent slip and only one were left, deformation of a specimen of this metal would be much more difficult and its Rockwell "hardness" would increase.

It is just this sort of keying which is provided by the structure of ordered AuCu according to the theory outlined in the preceding pages. As can be seen in Fig. 8, only one of the sets of octahedral planes runs parallel to the layers in which the ordered structure has a constant orientation; the other octahedral planes cut across these layers. Slip on the planes parallel to the layers should be easier than on the others, since interatomic distances do not change with position in these planes, and the structure fits together after a glide of one interatomic distance just as well as it did before. Slip on planes which cut across layers of constant orientation should be difficult, since the interatomic distances do change from place to place in these planes and the structure cannot fit together after gliding. It is to be expected, therefore, that even a little ordering of the kind that occurs in AuCu would produce an increase in resistance to deformation, that is, in "hardness".

The theory of the ordering of AuCu is, therefore, in the enviable position of explaining successfully the results of all the experiments performed in this investigation. Inasmuch as the age hardening in these alloys can be completely explained in terms of the effects of an ordering reaction, it is logical to call it "order hardening", as is done in the title of this paper.

Order hardening can be most easily distinguished from other kinds of age hardening by means of X-ray diffraction patterns. The initial changes in the intensities of the reflections, their subsequent broadening and splitting, and finally the appearance of superstructure lines as aging progresses are very characteristic of an ordering process during which the unit of structure changes shape. If such a sequence of X-ray diffraction patterns is associated with the age hardening of a metal, one can safely say that the process is one of order hardening.

The rippled appearance of polished and etched grains is also rather characteristic of order hardening and such a microstructure should lead to the suspicion that an ordering reaction is taking place. This appearance is to be found here and there in the literature on

photomicrographs of various alloy systems. It is hoped to investigate some of these systems for order hardening. Preliminary results on a 27 weight per cent molybdenum in nickel alloy indicate strongly that its age hardening takes place through an ordering reaction.

ACKNOWLEDGMENT

The author is indebted to many members of the staff of the Research Laboratory of the General Electric Company for their criticism and advice during the period in which this paper was taking form. In particular, great credit is due to E. R. Parker, R. Smoluchowski, and H. A. Liebhafsky for reading the manuscript and making valuable suggestions, most of which were included in the text.

It is also a pleasure to acknowledge the painstaking and skillful assistance of George H. Smith, who prepared the X-ray diffraction patterns, and of Harriette E. Rockwell, who carried through the difficult metallography.

## DISCUSSION

E. C. BAIN:[8] All will agree that Dr. Harker has ably presented and defended his thesis. The paper has, it seems to me, an especial appeal for two reasons:

The first is, that for beginners in the X-ray crystallographic technique, the paper is in itself an excellent educational text on the subject.

The second reason is that the crystal structure investigated is tetragonal—changing to and from the cubic. Every day there are hundreds of tons of tetragonal metal secured by quenching which thereafter is caused to restore itself to the cubic by heating. I refer, of course, to martensitic hardening of steel by quenching and to its subsequent tempering. Perhaps the parallel is closer than first appears.

I should like to ask Dr. Harker a question. It seems to me that even in the final state of affairs in his specimens (wherein he logically proposes successive layers on the 111 planes of the three orientations of tetragonal lattice separated by layers of the cubic structure) one would really expect a series of "tetragonality gradients", each of his blocks actually shading gradually into the next. Would this be correct?

I think Dr. Harker would be willing to answer questions as to his technique in obtaining the clear crystallograms and on the details of their interpretation. Many of you will wish to read the paper very carefully since he has, in his presentation today, omitted a part which deals with definitions. Finding, as we do, conditions of atomic arrangements which do not by any means automatically

[8]Vice-president, Carnegie-Illinois Steel Corp., Pittsburgh.

fit our concepts of yesterday, we are forced to review our definitions. Dr. Harker undertakes to fit ordered solid solutions into the pattern of phase change and you will find the discussion entertaining whether or not you agree with it in entirety.

A great deal of credit belongs to Dr. Harker for the clarity of his crystallograms and for all his illustrations; they are models of graphic presentation. All too rarely do structure diagrams show so clearly the geometry they are intended to portray. These of Dr. Harker may well be used for teaching purposes.

G. M. FOLEY:[9] I hate to ask a silly question but is there any explanation you could give as to why the diagrammatic representation of copper and gold atoms should be tetragonal when it looks as if the thing would be isotropic?

JOSEPH C. DANEC:[10] Can Dr. Harker show us a diffraction pattern of the usual type of precipitation hardening that we normally think of?

WILLIAM L. FINK:[11] Photomicrographs indicate that approximately the same structure is produced by precipitation hardening except that the lines do actually cross each other. Perhaps that is one distinction between this type of hardening and precipitation hardening.

I think the distinction between the two types of hardening will show up better, however, at a later stage. Dr. Harker mentioned that the indications of the two processes are very similar in the early stages. Perhaps more attention should be given to the later stages where the differences between the two methods are more clearly revealed.

CHARLES S. BARRETT:[12] Is it possible to conclude from your experiments whether this "order hardening" is due to stresses within or at the boundaries of the layers, or, on the other hand, to the formation of boundaries that are stress-free—a hardening from refining the grain size. Do the alloys overage? If softening occurs during prolonged annealing and without a change in the dimensions of the markings in the microstructure, it would strongly suggest that stresses from lattice coherency are the true cause of the hardening. In this case, the hardening and softening cycle here would closely resemble the cycle in certain precipitation hardening alloys where hardening seems to be associated with stresses accompanying the formation of an unstable precipitate that coheres, atom for atom, with the matrix solid solution and where overaging accompanies the release of these stresses.[13]

## Author's Reply

Knowing, as I do, how difficult it is to arrange to attend even a technical meeting in these busy times, I wish to express my gratitude to all those who were interested enough to come to hear my paper. I am delighted to have provoked such able discussion and regret that I am unable to give completely satisfactory answers to much of it—my knowledge being what it is.

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[9]Research engineer, Battelle Memorial Institute, Columbus, O.

[10]Grinding engineer, Norton Co., Worcester, Mass.

[11]Chief of physical metallurgy division, Aluminum Research Laboratories, New Kensington, Pa.

[12]Associate professor, Department of Metallurgy, Carnegie Institute of Technology, Pittsburgh.

[13]A. H. Geisler, C. S. Barrett, and R. F. Mehl, *Transactions*, American Institute of Mining & Metallurgical Engineers, Vol. 152, 1943, p. 182.

The gracious remarks of Dr. Bain were particularly pleasant for a newcomer in metallurgy to hear. I had hoped that my analysis of the age hardening of gold-copper alloys might apply to other, more important systems. If it can be applied to the problems connected with martensite, as Dr. Bain suggests, this hope will have been more than fulfilled. I also thank Dr. Bain for his flattering comment on my illustrations.

I shall now try to give answers to the technical questions asked during the discussion.

The AuCu structure is tetragonal because one of the original cube directions of the structure is perpendicular to planes that contain only gold or only copper atoms, while the other two original cube directions are perpendicular to planes that contain both gold and copper atoms. A structure which can be described by three mutually perpendicular axes, one of which is different from the other two, is called tetragonal.

In moving from point P to point Q in Fig. 8, the direction of the tetragonal axis is shown as changing suddenly at the boundaries between layers of constant orientation; this, of course, is physically impossible. A more likely situation is crudely shown in Fig. 10, where layers of disordered material separate the ordered layers of different orientation. Dr. Bain has pointed out that these disordered regions probably contain "tetragonality gradients." This phrase expresses very elegantly the only state of affairs which can actually exist, since it would be almost as difficult for a tetragonal layer to fit perfectly with a competely disordered layer as with another tetragonal layer of different orientation.

A tetragonality gradient might occur as follows:

As the boundary of an ordered layer is approached, the segregation of gold and copper atoms into alternate planes becomes less marked, until, at the point midway between two ordered layers, the two kinds of planes become physically indistinguishable. On moving farther in the same direction a new set of planes starts to show segregation, which becomes more marked, until, when the next ordered layer is reached, it is the maximum possible for the composition of the specimen. Plateaus of tetragonality are thus connected smoothly by tetragonality gradients.

The concept of tetragonality gradients provides a framework on which to shape my discussion (I can hardly call it an answer) of Dr. Barrett's searching questions. At each point in a tetragonality gradient two opposing tendencies exist: one of these is that of the alloy to attain its greatest possible order, the other is the necessity of smoothly fitting together the ordered layers on each side of it. An abrupt change in orientation at the boundary between two tetragonal layers would necessitate great strains there—and their concomitant stresses—if the two layers are to fit "atom for atom." These strains could be completely eliminated if the ordering were reduced to the appropriate value at each point. ("Strain" I interpret as being a change in shape caused by a "stress." A change in shape caused by a change in atomic arrangement involves no "stress", hence is not a "strain.") However, the equilibrium, strain-free state of order is higher than that existing in a tetragonality gradient, so that the material at a point in the gradient will order more than the reduced amount required to eliminate all strain. This ordering will continue until, at equilibrium, the strain energy balances the free energy decrease due to increasing the order. On the basis of

this picture, therefore, there should be some strain in the boundary between two ordered layers of different orientation. The stresses in this boundary material are not great enough, however, to account for the change in shape of the unit cell of the alloy as a tetragonality gradient is traversed.

Interference with slip must be due to irregularities in the slip planes. When these irregularities are caused by variations in shape of the metal's unit cell from place to place, it can usually be said that slip is being made difficult by strains; that is: the metal is strain hardened. Since strains are caused by stresses, it can be said that the hardness of an inhomogeneously strained metal is due to stresses.

The hardness of a metal increases as its grain size diminishes, due in all likelihood to the discontinuities of slip direction across the grain boundaries. Here the interference with slip is due to irregularities in the slip planes—of a rather extreme kind—but, in this case, without the presence of stresses.

In the case of the ordered AuCu alloys, the irregularities in the slip planes are greater than can be accounted for by the stresses probably present—as argued above—so that the hardness of these materials is not entirely due to stresses. Neither, on the other hand, can changes in slip direction from ordered layer to ordered layer be given the sole credit for the hardness effects observed. The analysis I have just given of the state of affairs in ordered AuCu type alloys makes it seem probable to me that their hardness is due to a sort of hybrid between the stress effect and grain size effect.

That I have no experimental proof for my theory of a mechanism of hardening is a fate I share with many others.

I have not heated any of my specimens of gold-copper alloys longer than seven hours, during which time no decrease below the maximum hardness took place. This is not a long enough aging treatment to decide whether or not overaging occurs. It will be interesting to perform these experiments, and I am grateful to Dr. Barrett for suggesting them.

I have been asked by Mr. Danec to show the diffraction effects accompanying the type of precipitation hardening normally thought of. I am sorry to say that a not very thorough search of the literature has failed to locate such a set of diffraction patterns. While many "precipitation hardening" systems have been studied, none of the references I have read show a sequence of diffraction effects such as would be expected of a simple precipitation reaction. It is true that prolonged annealing of alloys capable of precipitation reactions gives rise to specimens whose X-ray diffraction patterns are a super-position of the patterns of the matrix and the precipitate, but during the early stages of "precipitation hardening" the diffraction patterns show a number of phenomena not to be expected from a process which consists in the separation of fine particles of a new substance from a matrix. Indeed, most of these so-called "precipitation hardening" processes show a sequence of X-ray diffraction effects very similar to those I have observed with the gold-copper alloys: there are changes in the widths and intensities of the lines of the matrix, without much change in their positions, and the lines of the precipitate do not appear until the hardening is well advanced. The actual process occurring is doubtless not that usually thought of. I am hoping to compare the early stages of "precipitation" hardening with "order" hardening by means of their X-ray diffraction effects, for I strongly suspect that the two processes may not be very different.

The question of Dr. Fink concerning the microscopic appearance of the alloys can be answered only by further metallographic work on many age hardening systems. It may well be that the crossing or not crossing of the lines in the ripple structure will determine the type of age hardening taking place in the alloy under consideration. However, other order hardening systems must be identified and examined before such a generalization can be made. It seems to be true that the lines do not cross each other in the gold-copper alloys I have examined.

# THE EMISSIVITY OF MOLTEN STAINLESS STEELS

By George N. Goller

*Abstract*

*A systematic study of the emissivity of molten stainless steels is presented. The 0.40 emissivity value usually assumed for molten steels results in corrected optical pyrometer readings which are misleading when applied to stainless steels.*

*By practically simultaneous thermocouple and optical pyrometer readings obtained from a number of heats melted in an experimental induction furnace, emissivities ranging from 0.40 to 0.75 were determined depending upon the analysis of the steel. The data are presented in the form of calibration charts for the optical pyrometer which can be used when measuring molten steel temperatures during the tapping and pouring operations in the mill.*

*Graphs indicating the effect of several alloying elements upon the emissivity of molten steel are included. It was found that with increasing chromium, manganese, titanium, or columbium contents the emissivity increases, while a decrease in emissivity occurs with increasing nickel, silicon, sulphur, or selenium plus phosphorus contents. No appreciable effect was noted from carbon or molybdenum.*

*An example from actual practice is also included to indicate the usefulness of this study.*

A STUDY of the literature fails to disclose any experimental data on the emissivity of molten stainless steels, nor in fact, any systematic data on the emissivity of alloy steels as a class.

In 1914, Burgess (1)* determined the emissivity of molten iron and steel in a hydrogen atmosphere by the use of a micropyrometer. The average value he obtained was 0.37. However, in 1917, Burgess (2) recommended that 0.40 be used in actual practice. This value is commonly used in the steel mill to make corrections in the optical pyrometer readings for a wide variety of steels, including certain alloy steels as well as stainless steels.

Several investigators have reported emissivity values for molten

*The figures appearing in parentheses pertain to the references appended to this paper.

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carbon steels since the early work of Burgess. The average values reported by Leiber (3), Todd (4), and the Tetsu-to-Hagane (5) range from 0.4 to 0.45.

At the plant of the steel company with which the writer is connected, the use of immersion thermocouples to determine molten steel temperatures was begun in an experimental way about five years ago. The technique eventually adopted was the quick immersion method developed in England by Schofield and Grace (6).

As a result of this thermocouple work, it soon became apparent that it was a matter of considerable importance to determine the emissivity of the different stainless steel grades in order to obtain strictly comparable optical pyrometer readings, as, for example, in the case of pouring practice.

## Procedure

Seventeen-pound heats were melted in a high frequency induction furnace (Ajax-Northrup, 35 KVA) using a fused magnesia crucible. The true temperature of the metal was determined with a platinum-platinum + 13 per cent rhodium thermocouple protected by a silica tube which was immersed in the metal bath. This method of measuring molten steel temperatures is fully described in the transactions of the British Iron and Steel Institute (6). The thermocouple voltage was measured with a Leeds and Northrup high-precision portable laboratory potentiometer, which was checked for accuracy against a Leeds & Northrup Type K2 precision potentiometer.

The platinum thermocouples used in this study were frequently checked against a standard couple of the same type which had been calibrated by the U. S. Bureau of Standards at one millivolt intervals from 2 millivolts to 17 millivolts.

The brightness temperature or apparent temperature of the metal was obtained with an optical pyrometer which was sighted on the clear surface of the molten steel at the lip of the furnace as the metal was being poured (Fig. 1). Any oxide film which formed on the metal was broken by the pouring action, thereby exposing clear metal. However, on such grades as 27 Cr-20 Ni, 16 Cr-2 Ni, and 18-8 Ti, it was extremely difficult to get readings on clear unoxidized metal because of rapid oxidation of the surface.

Molten steel when first exposed to the air has a clean, clear surface. An oxide film forms on the liquid metal at a rate which de-

pends upon the analysis, the degree of deoxidation and the temperature. Actually, the film is at the same temperature as the metal, but appears to be much hotter due to the higher emissivity of the oxides. Experience has shown that optical pyrometer readings taken on this

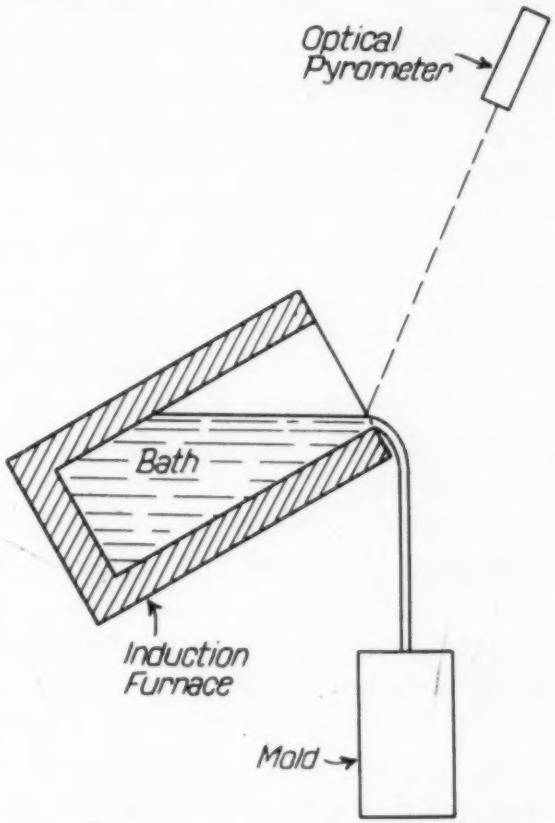


Fig. 1.—Method Used to Obtain Optical Pyrometer Readings.

film range from 100 to 200 degrees Fahr. higher than those taken on clear metal. Therefore, in order to obtain optical temperatures which can be used successfully for comparative purposes, care must be taken to distinguish between the "dark" and "bright" surfaces. Readings taken on the clear or "dark" metal are preferred because its emissivity varies less than that of the oxide film.

Care was taken not to sight on any part of the metal bath which might result in erroneous readings due to reflections from the furnace wall. Precautions were also taken to avoid smoke and vapors which would result in low readings.

In the course of the investigation, a Leeds and Northrup and a Pyro optical pyrometer were both used and found to yield identical results within the range of experimental error. However, the Pyro

was favored in this investigation because it afforded greater ease in obtaining a brightness match on small areas of clear metal. This instrument was regularly checked against a Leeds and Northrup optical pyrometer used as a standard and previously calibrated with the aid of a black-body furnace and the Bureau of Standards thermocouple. The check was made by comparing readings taken with the standard and the working pyrometers on a tungsten ribbon filament or "strip" lamp heated by means of constant current supplied by sixteen 6-volt, 180 ampere-hour storage batteries connected in parallel.

The power supply to the induction furnace remained on while the thermocouple reading was obtained and for approximately ten seconds thereafter, this time being required to remove the couple from the bath. The power input had been previously adjusted to such a value that the temperature of the bath was increased 5 to 10 degrees Fahr. in this time. The power was then shut off and the metal poured from the furnace into a mold. The optical pyrometer measurement was made at the beginning of this pouring. The total time elapsing between the thermocouple and the optical pyrometer readings was approximately twenty seconds. It was determined by experiment that the bath lost only 5 to 10 degrees Fahr. during the ten seconds between the time the power was shut off and the time the optical reading was obtained. This loss was compensated for by the temperature increase after the thermocouple measurement was made, thereby making the temperature of the metal, for all practical purposes, the same when the thermocouple and optical pyrometer readings were taken.

Measurements, as described above, were made on eight heats of 18 per cent chromium-9 per cent nickel and six heats of 16 per cent chromium steels, thereby establishing the calibration of the optical pyrometer for these steels. The plotting of calibration curves for the two steels resulted in parallel straight lines. Fewer readings were, therefore, necessary for other grades, since all apparently had similar characteristics. Table I lists typical analyses of the steels studied.

## Discussion

The data obtained in this study are best presented by plotting the true temperature (thermocouple) against the apparent temperature (optical pyrometer) for each grade, as shown in Figs. 2 and 3.

**Table I**
**Analyses of Steels Studied**

| Steel No. | Steel | C | Mn | P | S | Si | Cr | Ni | Mo | Cb | Ti | Se |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Carbon Steel | 0.090 | 0.42 | ..... | ..... | 0.07 | Nil | Nil | .... | .... | .... | .... |
| | Ingot Iron | 0.020 | 0.02 | ..... | ..... | Nil | Nil | Nil | .... | .... | .... | .... |
| 2 | 12 Cr–Sulphur | 0.089 | 0.39 | 0.015 | 0.334 | 0.27 | 12.21 | 0.19 | 0.40 | .... | .... | .... |
| 3 | 5 Cr | 0.177 | 0.45 | 0.013 | 0.026 | 0.32 | 5.22 | 0.13 | 0.52 | .... | .... | .... |
| 4 | 12 Cr | 0.093 | 0.39 | 0.012 | 0.021 | 0.25 | 12.00 | 0.21 | 0.44 | .... | .... | .... |
| 5 | 16–2 | 0.144 | 0.41 | 0.018 | 0.022 | 0.45 | 16.44 | 1.82 | .... | .... | .... | .... |
| 6 | 16 Cr | 0.067 | 0.47 | 0.012 | 0.018 | 0.34 | 16.27 | 0.40 | .... | .... | .... | .... |
| 7 | 27 Cr | 0.126 | 0.43 | 0.026 | 0.021 | 0.67 | 26.80 | 0.33 | .... | .... | .... | .... |
| 8 | .35C–13 Cr | 0.424 | 0.36 | 0.015 | 0.025 | 0.36 | 13.07 | 0.29 | 0.33 | .... | .... | .... |
| 9 | 1.00 C–17 Cr | 1.24 | 0.58 | 0.012 | 0.030 | 0.78 | 17.39 | 0.35 | 0.40 | .... | .... | .... |
| 10 | 17 Cr–2 Si | 0.061 | 0.67 | 0.015 | 0.026 | 2.15 | 16.83 | 0.30 | .... | .... | .... | .... |
| 11 | 2 Cr | 0.087 | 0.36 | 0.013 | 0.020 | 0.14 | 1.96 | 0.07 | .... | .... | .... | .... |
| 12 | 18–9 Sulphur | 0.071 | 0.65 | 0.016 | 0.326 | 0.38 | 18.54 | 9.59 | 0.38 | .... | .... | .... |
| 13 | 18–9 | 0.056 | 0.48 | 0.016 | 0.019 | 0.38 | 17.98 | 9.01 | .... | .... | .... | .... |
| 14 | 27–20 | 0.106 | 1.60 | 0.023 | 0.016 | 0.48 | 26.47 | 21.67 | .... | .... | .... | .... |
| 15 | 18–12–3 Mo | 0.049 | 1.58 | 0.019 | 0.010 | 0.52 | 17.05 | 12.42 | 2.43 | .... | .... | .... |
| 16 | 18–10 Cb | 0.070 | 1.27 | 0.020 | 0.020 | 0.55 | 17.96 | 11.01 | .... | 0.89 | .... | .... |
| 17 | 18–10 Ti | 0.054 | 1.32 | 0.025 | 0.018 | 0.79 | 18.34 | 10.87 | .... | .... | 0.35 | .... |
| 18 | 18–9 Se | 0.071 | 0.87 | 0.156 | 0.021 | 0.60 | 18.50 | 8.74 | .... | .... | .... | 0.29 |
| 19 | 18–9–2 Mn | 0.070 | 2.21 | 0.014 | 0.026 | 0.54 | 17.99 | 8.83 | .... | .... | .... | .... |
| 20 | 18–9–4 Mn | 0.087 | 3.77 | 0.027 | 0.020 | 0.60 | 18.80 | 8.56 | .... | .... | .... | .... |
| 21 | 18–9–7 Mn | 0.087 | 7.29 | 0.035 | 0.015 | 0.67 | 18.45 | 8.62 | .... | .... | .... | .... |
| 22 | 18–9–1 Si | 0.075 | 0.67 | 0.012 | 0.023 | 1.04 | 18.61 | 8.77 | .... | .... | .... | .... |
| 23 | 18–9–1.5 Si | 0.064 | 0.66 | 0.015 | 0.021 | 1.48 | 18.79 | 9.95 | .... | .... | .... | .... |
| 24 | 18–9–2 Si | 0.071 | 0.70 | 0.013 | 0.021 | 2.23 | 18.77 | 8.71 | .... | .... | .... | .... |
| 25 | 18–9–4 Si | 0.057 | 0.63 | 0.014 | 0.020 | 4.18 | 19.33 | 8.67 | .... | .... | .... | .... |
| 26 | 18–4 | 0.074 | 0.63 | 0.013 | 0.020 | 0.65 | 18.72 | 4.21 | .... | .... | .... | .... |
| 27 | 15–35 | 0.60 | 0.64 | 0.012 | 0.018 | 0.95 | 14.91 | 34.68 | .... | .... | .... | .... |

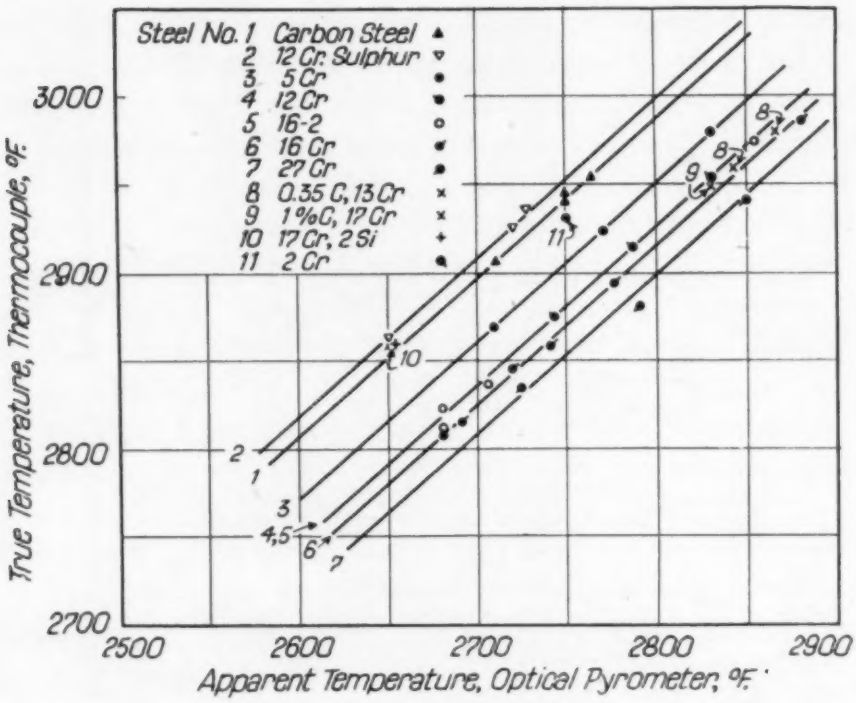


Fig. 2—Calibration Chart for Optical Pyrometer; Molten Straight Chromium Steels.

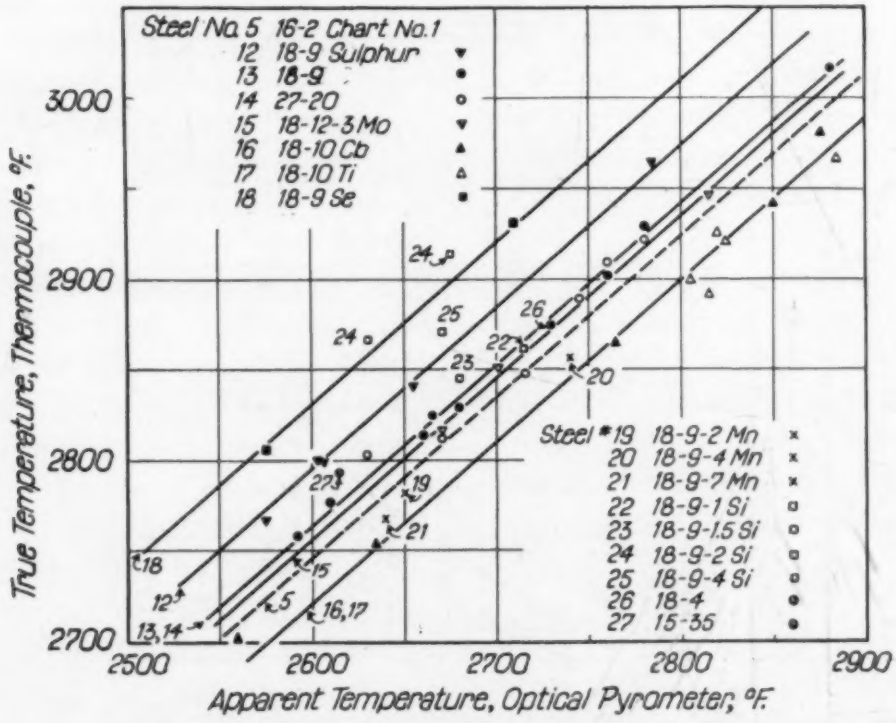


Fig. 3—Calibration Chart for Optical Pyrometer; Molten Chromium-Nickel Steels.

These can be used as calibration charts for the optical pyrometer when measuring the temperature of molten steels during the tapping and pouring operations. If the analysis is known, the true temperature corresponding to the optical pyrometer reading can be obtained from the charts.

It is quite apparent that for different steels, the optical pyrometer gives different readings at the same true temperature. This indicates a variation in emissivity with analysis. Emissivities ranging from 0.40 to 0.75 were obtained as compared to the 0.4 usually accepted for molten steels. The emissivity is calculated from the following equation when the true and apparent temperatures are known:

$$\frac{1}{T_t} - \frac{1}{T_a} = \frac{\lambda \log_e E_\lambda}{C_2}$$

in which $T_t$ = True temperature, °Kelvin (Thermocouple),
$T_a$ = Apparent temperature, °Kelvin (Optical pyrometer),
$\lambda$ = Effective wave length of filter in optical pyrometer (.65 $\mu$),
$C_2$ = Second radiation constant, 14,360 (7)
$E_\lambda$ = Emissivity.

The effect of analysis upon the emissivity can be noted in Fig. 4 which was derived from the data in Figs. 2 and 3 and the equation given above. Actually this calculation resulted in flat S-shaped curves, but since a difference of only 10 degrees at 2900 degrees Fahr. (1595 degrees Cent.) will result in a variation of approximately 0.03 in emissivity, it was decided that for the purpose of illustration an average straight line would suffice. With increasing chromium and manganese contents, the emissivity was found to increase while the carbon content had little effect. This phenomenon was also noted by Sosman (8), (9), Sordahl (8), Naeser (10), and Guthman (11). However, the emissivity was found to decrease as the nickel and sulphur content increased. Fig. 4 also indicates an increase in emissivity with increase in temperature.

After a thorough study of the data, it was found possible to produce curves showing the effect of chromium, nickel, manganese and silicon upon the emissivity of molten steel. The effect of chromium is illustrated in Fig. 5. The emissivity increases considerably with chromium up to approximately 30 per cent, above which the rise apparently becomes much less.

The emissivity of molten 18-per cent chromium steel decreases with increased nickel content, as shown in Fig. 6. Up to 4 per cent the effect is marked, beyond which the decrease is slight.

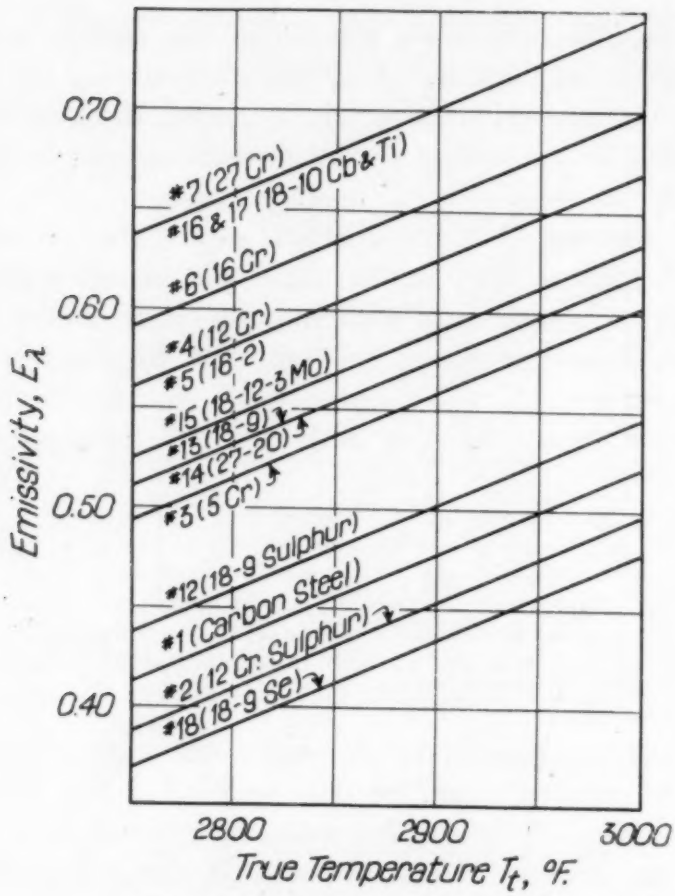


Fig. 4—Emissivities of Various Stainless Steels versus the True Temperature.

The emissivity of molten 18 per cent chromium-9 per cent nickel steel increases greatly as the manganese is increased to 2 per cent (Fig. 7). A small increase takes place from 2 to 4 per cent manganese, but from 4 to 8 per cent no further change in emissivity takes place.

Fig. 8 indicates the effect of silicon upon the emissivity of molten 18 per cent chromium-9 per cent nickel steel. Silicon has little or no effect up to 1 per cent; however, a considerable drop occurs between 1 and 2 per cent. The same effect was observed in a straight 16 per cent chromium steel. Above 2 per cent silicon, it becomes exceedingly difficult to obtain reliable optical pyrometer measurements due to the presence of a quick-forming oxide film. However, a fairly reliable set of readings at 4 per cent silicon indicates an increase in emissivity.

Carbon influences emissivity very little, if at all. Readings obtained on a 13 per cent chromium steel with 0.42 per cent carbon

were identical to those of a 0.10 per cent carbon-13 per cent chromium steel. However, one set of readings taken on a 17 per cent chromium steel with 1.24 per cent carbon indicated a very slight decrease in emissivity, although this may have been due to the presence of 0.78 per cent silicon.

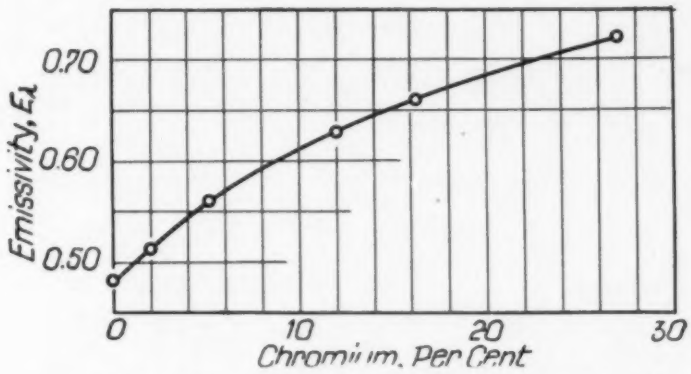


Fig. 5—The Effect of Chromium Content Upon the Emissivity of Molten O.10 Carbon Steel at 2900 Degrees Fahr.

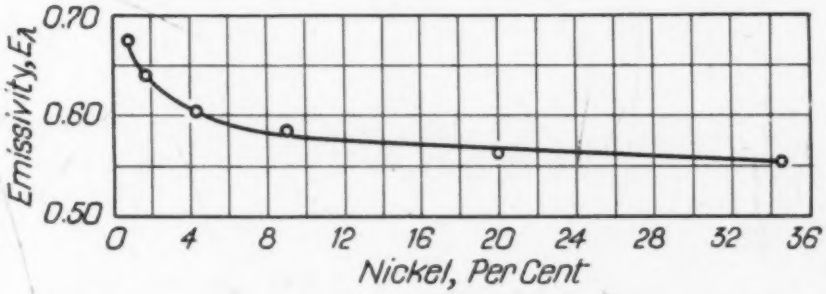


Fig. 6—The Effect of Nickel Content Upon the Emissivity of Molten 18 Per Cent Chromium Steel at 2900 Degrees Fahr.

The presence of such elements as columbium and titanium resulted in an increase in emissivity, while molybdenum apparently had very little effect.

The results of this study indicate that the individual effect of the elements present on the emissivity are additive, thereby making it possible to estimate closely the emissivity of a new grade of steel.

It is possible that the influence of analysis upon the emissivity of molten steel is due to the formation of various types of nonmetallic inclusions in the steel and the rapidity with which an oxide film tends to form on the metal surface. This film may be a transparent oxide such as silica, or possibly even a gas such as the sulphur dioxide which is given off from a high sulphur heat.

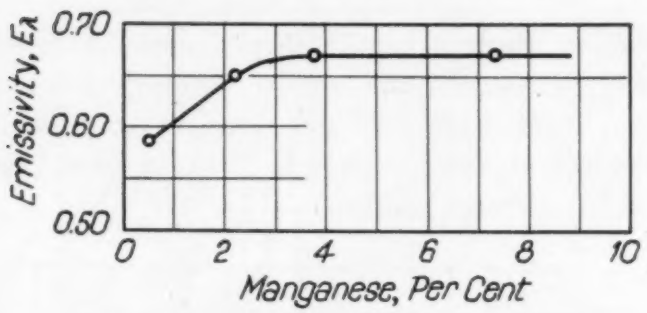


Fig. 7—Effect of Manganese Content Upon the Emissivity of Molten 18 Per Cent Chromium-9 Per Cent Nickel Steel at 2900 Degrees Fahr.

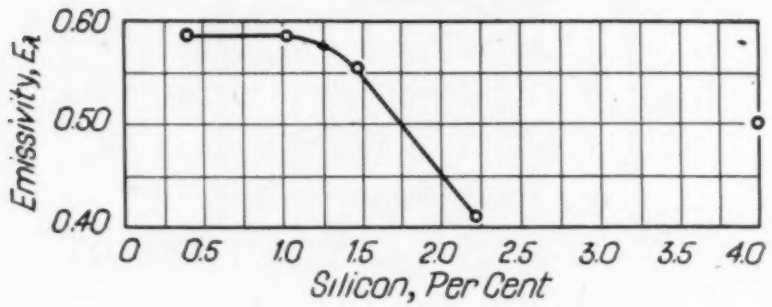


Fig. 8—The Effect of Silicon Content Upon the Emissivity of Molten 18 Per Cent Chromium-9 Per Cent Nickel Steel at 2900 Degrees Fahr.

A practical application of this work is shown in the following tabulation obtained from a fifteen-ton commercial heat of free-machining 12 per cent chromium steel (Type 416). The metal leaving the furnace during tap was a 12 per cent chromium steel. An addition of sulphur was made as it entered the ladle, resulting in a high sulphur 12 per cent chromium steel during the pouring of the ingots.

| | Apparent Temp. (Optical) | Optical Correction | True Temperature | Corrected Temp. (Fig. 2) |
|---|---|---|---|---|
| Platinum thermocouple in furnace two minutes before tap | .... | .... | 2912° F. | .... |
| During tapping of heat (12% chromium) | 2800° F. | 125° F. | .... | 2925° F. |
| During pouring of heat (12% Cr, FM)* | 2620° F. | 213° F. | .... | 2833° F. |
| Temperature loss in ladle | 180° F. | .... | .... | 92° F. |

*After sulphur addition.

The uncorrected optical readings indicate a drop of 180 degrees Fahr. in the ladle between the time of tapping and the pouring. However, when using the calibration chart to correct these readings, the actual temperature drop in the ladle is only 92 degrees Fahr., which is normal for this steel. A similar condition exists when manganese additions are made in the ladle. The close agreement

between the corrected optical temperature and the temperature obtained two minutes before tap with the quick immersion platinum thermocouple (6) should be noted. By making use of the calibration charts established in this study, the results obtained with the optical pyrometer in our melt shop became much more useful than in the past.

It is hoped that the results of this study constitute a contribution to the field of optical pyrometry, since very little data have been published concerning the effect of various alloying elements upon the emissivity of molten steel. The steel industry has assumed an emissivity of 0.4 for molten steel, but this value seems to be somewhat low, resulting in corrected optical readings which are too high even for some carbon steels. The emissivity of molten plain carbon steel obtained in this study ranged from 0.43 at 2800 degrees Fahr. (1540 degrees Cent.) to 0.52 at 3000 degrees Fahr. (1650 degrees Cent.). This compares favorably with the values reported by other investigators.

## Summary

This study shows that the 0.4 emissivity, usually assumed for molten steels, does result in corrected optical pyrometer temperatures which are too high for some steels. The instrument was calibrated for a number of stainless steels by essentially simultaneous thermocouple and optical readings. Emissivities ranging from 0.40 to 0.75 were found, depending upon the analysis. The effect of increasing concentrations of various alloying elements upon the emissivity of molten steel is listed in the following tabulation:

| Element | Emissivity |
|---|---|
| Cr | Increases |
| Mn | Increases |
| Ti | Increases |
| Cb | Increases |
| Ni | Decreases |
| Si | Decreases |
| S | Decreases |
| Se + P | Decreases |
| C | No appreciable effect |
| Mo | No appreciable effect |

The calibration charts make it possible to obtain temperature readings with the optical pyrometer on molten steels during the tapping and pouring operations which are of greater practical use than in the past.

ACKNOWLEDGMENT

In addition to A. L. Feild, Technical Director of Rustless Iron and Steel Corporation, the author wishes to acknowledge his indebtedness to the other members of the staff for their valuable suggestions and assistance, particularly to L. F. Weitzenkorn and H. W. Cobb. L. F. Weitzenkorn, Research Engineer, took an active part in the early phase of the general investigation on molten steel temperatures and made many valuable suggestions. H. W. Cobb, Research Physicist, was responsible for the accurate calibration of temperature measuring instruments and equipment employed in the investigation, and contributed valuable technical advice in the course of the investigation.

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## DISCUSSION

**Written Discussion:** By W. E. Forsythe and E. Q. Adams, Lamp Department, General Electric Co., Cleveland.

Mr. Goller's paper gives data that are an interesting addition to the field of the measurement of the temperature of metals and alloys. The values given would have carried more weight if arrangements had been made to measure the temperature of the molten metal with the thermocouple, and its brightness temperature with the optical pyrometer, at the same time. However, the precautions taken to minimize the error due to this cause seem satisfactory.

A table giving the emissivity of the different alloys for at least one temperature, and an explicit statement of the temperature coefficient of emissivity, should be included in the paper. We are glad that the author explained the necessity of getting and keeping a clean surface of the molten alloy because this is very important in studying the emissivity of any metal. Mr. Goller's results on the emissivity of the alloys of iron show that the addition of metals that come before iron in the periodic table increases its emissivity and the addition of metals that follow iron in the periodic table decreases the emissivity. The elements with more outer electrons than iron have a lower emissivity, i.e., a higher reflectivity than iron. According to the electron theory metallic reflection is attributed to electrons not in closed shells.

Within the error of measurement, the better-determined curves relating emissivity to composition are rectangular hyperbolas, suggesting an adsorption of the alloying elements onto the surface in accordance with the Langmuir adsorption law. As will be seen from the accompanying table, all the added elements except carbon and nickel have atomic volumes greater than that of iron, a factor which would favor adsorption onto the surface.

In default of measurements of the effect on emissivity of the separate elements, it has not been thought advisable to attempt to extrapolate for the maximum possible effect. The greatest percentages of carbon and molybdenum added were small, hence the results shown for alloy No. 15 in Fig. 4 do not seem to substantiate the statement in the table of the summary that molybdenum has no effect on the emissivity. On account of the low solubility of manganese sulphide in molten iron, it is possible that the data on sulphur represent (at least in part) the effect of removing manganese.

This paper shows the necessity for more work in this field in order to obtain all the data that one would need for this purpose. In particular, more work should be done on the effect on emissivity of the separate metals before the statement could be made that the changes in emissivity are additive.

**Maximum Observed Effect on Emissivity at 2900 Degrees Fahr. of Various Alloying Components of Stainless Steel**

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Atomic Volume | | | | | | | | | | | | 3.4 | | | |
| Element, Atomic No. | | | | | | | | | | | | C6 | | | |
| Change in Emissivity | | | | | | | | | | | | —0.03 | | | |
| Atomic Volume | | | | | | | | | | | | 11.4 | | 16. | |
| Element, Atomic No. | | | | | | | | | | | | Si14 | | P15 | S16 |
| Change in Emissivity | | | | | | | | | | | | —0.18 | | | —0.17 |
| Atomic Volume | 10.7 | | 7.6 | 7.4 | 7.1 | | 6.7 | | | | | | | | 18.5 |
| Element, Atomic No. | Ti22 | V23 | Cr24 | Mn25 | Fe26 | Co27 | Ni28 | Cu29 | Zn30 | Ga31 | Ge32 | As33 | Se34 | | |
| Change in Emissivity | +.12 | | +0.25 | +0.09 | | | —0.11 | | | | | | —0.14 | | |
| Atomic Volume | | 11.8 | 9.3 | | | | | | | | | | | | |
| Element, Atomic No. | | Cb41 | Mo42 | | | | | | | | | | | | |
| Change in Emissivity | | +0.12 | +0.02 | | | | | | | | | | | | |

**Written Discussion:** By John W. Juppenlatz, chief metallurgist, Lebanon Steel Co., Lebanon, Pa.

We have in the foundry industry for some time been confronted with the problem of obtaining optical readings on molten metals such as cast iron and

steel. It has been recognized that the readings as obtained were not true temperatures and that comparisons of the relative temperatures as obtained were not too good.

Mr. Goller's work gives us true temperatures and their emissivity corrections per optical pyrometer, which is certainly helpful in determining the true temperatures of molten steel. However, I am wondering if for all practical purposes that a relative temperature rather than a true temperature does not work equally as well in production practices.

Our average pouring temperature for chromium and the nickel-chromium series of austenitic steels, by the use of the optical pyrometer with corrections, is in the neighborhood of 2950 to 3000 degrees Fahr. (1620 to 1650 degrees Cent.) for small castings. Experience has shown that these optical figures enable us to satisfactorily pour the smaller types of castings. Of course, we realize that these temperatures are neither true nor possibly anything better than relative. Our greatest problem at these temperatures is the objectionable smoke feature.

Another production problem involves the oxide film formation which occurs at some of the lower temperatures. Optical readings often seem to be misleading, even though attempts are made to break the oxide film and obtain a good reading. Possibly Mr. Goller would recommend corrections to overcome this oxide film formation.

I am very glad to see that some work has been done which enlightens us on the emissivity of stainless steel so that we may know how to apply the optical pyrometer in a more intelligent manner.

### Oral Discussion

JOHN R. GREEN:[1] Mr. Goller's paper is a valuable addition to the information on this subject of measuring alloy steel temperatures during melting operations. I would like to ask questions on some points which have come up in connection with work using radiation elements rather than optical elements in measuring molten metal temperatures. First, was the work done on the basis of measurements from the oxide film or an unoxidized metal surface? Previous work on molten iron, done by Dr. R. H. Koch and Dr. A. E. Schuh, has indicated the probability of more stable conditions when measuring the oxide film rather than the unoxidized metal, since the oxide film forms with extreme rapidity at these temperatures.

The second point, was there any indication of a break or change in the emissivity of the metal at a particular temperature or temperature span? Indications of this are being found in other investigations. The range or readings from the charts appeared to be between 2800 and 2925 degrees Fahr. (1540 and 1610 degrees Cent.).

Has any additional work been done above or below those values which would indicate that there is a drastic change of emittance values at certain temperatures for each composition?

DONALD L. CLARK:[2] I would like to know what make of optical pyrometer was used on these tests.

[1]Manager of Steel and Ceramic Division, Brown Instrument Company, Philadelphia.
[2]Melting superintendent, Simonds Saw & Steel Co., Lockport, N. Y.

MICHAEL TENENBAUM:[3] I would like to ask Mr. Goller what was the highest temperature that he read.

MR. GOLLER: In this work we read up as high as 3050 degrees Fahr., but I have gone to the limit of the platinum couple, 3225 degrees Fahr. However, I do not know whether such a reading is very reliable.

MR. TENENBAUM: What protection did you use?

MR. GOLLER: Silica.

MR. TENENBAUM: Did you have any trouble with melting at that temperature?

MR. GOLLER: The protection tube gets soft but its life is still fairly good.

### Author's Closure

I wish to thank Mr. Forsythe and Mr. Adams for their able discussion of this work. The chart shown in Fig. 4 can be used to indicate the emissivity of the various grades represented at any given temperature. If the emissivities are desired at 2900 degrees Fahr. (1595 degrees Cent.) they can easily be picked off of the chart. The coefficient of emissivity is merely the slope of the lines on the chart. When I said that carbon and molybdenum had no appreciable effect upon the emissivity, I should have added "within the limits of stainless steel composition."

Mr. Juppenlatz's comments are appreciated since they are of a practical nature. It is true that for practical purposes a relative temperature can be used in production provided the temperatures obtained for different grades are not compared. The use of uncorrected readings results in a separate temperature scale for each grade of steel.

We have done considerable work with immersion couples and consequently had to be able to obtain true temperatures with the optical pyrometer in order to make comparisons. Therefore, we have one temperature scale in our shop which is the true temperature. The necessity of this is illustrated in the example on page 248.

The temperature range at which chrome-nickel steels are poured at Mr. Juppenlatz's plant is high when compared to our practice, but this would seem necessary to pour small castings.

Smoke and vapors seem to be a problem in every shop to some degree. Readings taken through smoke or vapors are unreliable and must be disregarded. The presence of an oxide film at the lower temperatures makes it difficult to obtain a reliable optical reading. However, if it is not possible to sight on the clear metal as the film breaks during pouring, it may be worthwhile to obtain a reading on the film at its hottest point and make a correction of 25 to 50 degrees Fahr.

In answer to Mr. Green's question, all of the data were obtained on the basis of an unoxidized metal surface because I feel that the emissivity of the clear or "dark" surface varies less than that of an oxide film. Data were obtained over a range of 2700 to 3000 degrees Fahr. (1480 to 1650 degrees Cent.) and no break in the coefficient of emissivity was noted. A break will occur if no distinction is made between readings taken on clear or oxided metal. Above a certain temperature, which depends on the analysis, the surface of normally deoxidized steels

[3]Metallurgist, Inland Steel Co., E. Chicago, Ind.

is free from an oxide film. However, below this temperature an oxide film forms which will cause a sudden increase in the emissivity if the metal surface is not taken into account.

As to Mr. Clark's question, both the Leeds and Northrup and the Pyro type optical pyrometers were used with identical results. However, most of the data were obtained with the Pyro because it afforded greater ease in obtaining a brightness match on a small area of clear metal.

I agree with Messrs. Forsythe and Adams that this paper shows the necessity for more work in this field. The work covered in the paper was done on a commercial scale to aid an operating department. However, it was presented to stimulate interest in this subject with the hope that additional data will be obtained in the future, perhaps along the lines suggested by Messrs. Forsythe and Adams.

# QUENCHING RATE VERSUS GRAPHITE FORMATION IN PREQUENCHED WHITE CAST IRON

By Orien W. Simmons

*Abstract*

*That rapid cooling from above its critical temperature range will greatly accelerate the subsequent graphitization of a white cast iron has been known for several years. The present paper reports some studies which indicate the correlation of the cooling rate attained during the pretreatment with the distribution of the resultant graphite and the disappearance of the residual primary cementite.*

*It was found that a Rockwell hardness of 57 C or more attained by a cooling rate of more than 240 degrees Fahr. per second at 1300 degrees Fahr. (705 degrees Cent.) was necessary to give martensite which annealed into a structure having the very fine prequenched type of graphite. In a comparatively narrow cooling range of 170 degrees Fahr. to 130 degrees Fahr. per second at 1300 degrees Fahr. (705 degrees Cent.), resulting in Rockwell C hardness values of 56 to 54 respectively, the martensite is interspersed with a constituent appearing to be fine pearlite and the resultant graphite changes from the very fine prequenched type to a type that closely resembles that of ordinary malleable iron though somewhat finer and more numerous. From here until very slow cooling rates are reached, the increase in the graphite size is very gradual. The primary cementite decomposition appears to be at a rate directly proportional to the number of graphite nuclei present, probably because the greater number of nuclei presents more surface for the deposition of carbon from the dissociation of the dissolved carbide.*

IT has long been known that white cast iron will graphitize much more readily during the malleableizing cycle if it has been subjected to a previous quench from above its critical range. As early as 1927 patents on this phenomenon were issued to Saito and Sawamura (1), (2)[1] and to H. A. Schwartz (3), (4). Their subsequent publications in the literature disclosed what is generally known about

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

A paper presented before the Twenty-fifth Annual Convention of the Society, held in Chicago, October 18 to 22, 1943. The author, Orien W. Simmons, is research engineer, Battelle Memorial Institute, Columbus, Ohio. Manuscript received July 2, 1943.

this occurrence. Austin and Fetzer (5), and Austin and Norris (6), have found a somewhat analogous situation to exist in hypereutectoid steels, though in this case the graphitization occurs below the $A_1$ where the mechanism may be quite different from that known to act in the critical region. Very recently Hultgren and Edstrom (7) have reported their observation with this pretreatment, but their original article has been unavailable to the author because of the war.

These reports indicate that extremely small carbide particles are much less stable in the graphitizing region than are the coarser spheroidized or massive cementite particles. Also, an increase in the severity of the strains such as results from a higher or faster quench may undoubtedly increase the tendency to graphitize and produce finer and more numerous graphite.

Despite this information there is a lack of quantitative data correlating the severity of the quench with the size, shape, and rate of formation of the graphite resulting from the pretreatment.

## The Effect of Prequenching Upon the Malleablization of White Cast Iron

In the present paper some studies are reported which indicate the correlation between the as-quenched structure and the resultant graphite. It appears that the acceleration of the graphitization reaction is rather sensitive to slight changes in the quenching rate for it was noted that a variation of two Rockwell C numbers was sufficient to substantially alter the graphite, and a range of seven Rockwell C numbers covered the whole gamut of graphite sizes obtainable by graphitizing at temperatures above the critical.

To obtain comparable quantitative results on material of this sort it is necessary either to repeat the observation many times or to use materials which are exactly identical. The latter condition is very difficult to set forth because of the inherent segregation resulting during freezing of the metal. However in this investigation such difficulties were minimized by using specimens from the same cast bar for all determinations and by a subsequent check on a duplicate bar handled in a similar manner.

### Procedure

For this investigation a white cast iron cylinder, three-fourths inch in diameter by three inches long, was ground to remove the as-

cast surface and to face off one end smooth and normal to the longitudinal axis. The cylinder was then immersed in a bath of molten lead for ten minutes at the end of which time the temperature of the lead bath measured with an immersion thermocouple was 1635 degrees Fahr. (890 degrees Cent.). The specimen was then removed and subjected to a quench with a stream of water at 75 degrees Fahr. directed against the ground end in a manner following the procedure employed for the end-quench hardenability test.

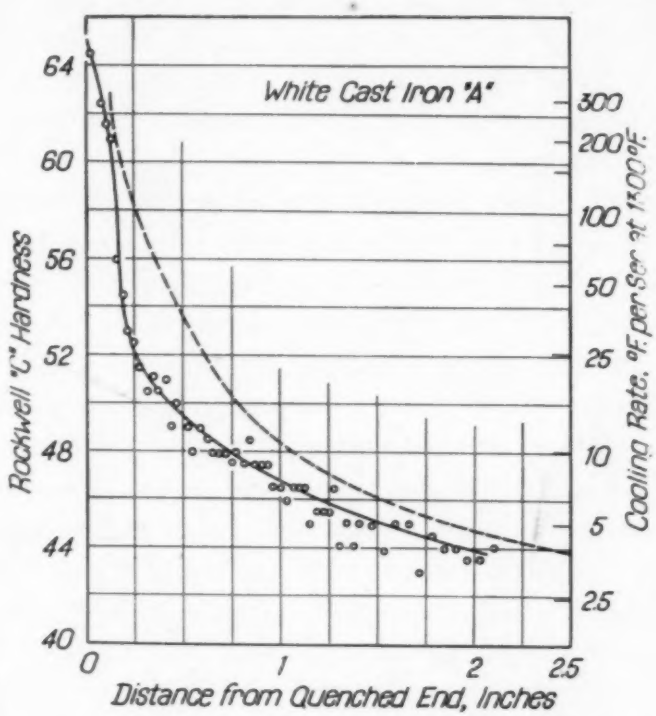



Fig. 1—Correlation of the Cooling Rate of Steel (Hill) with the Hardness Values of Quenched White Cast Iron, Each Plotted Versus its Location in the End-Quenched Specimen. (— — — —, Hill) (o————o, White Cast Iron.)

After the bar was quenched it was sectioned longitudinally into four quarter-sections each having identical cooling rates at corresponding points along the length measured from the quenched end. One of the quarters was then placed upon a surface grinder and a flat was ground parallel to one of the longitudinal cut faces and about one-half as wide. The piece was then lightly ground on the opposite face left by the abrasive cutting wheel to remove any trace of glazed surface that might have been left during sectioning. Rockwell C readings were made on the latter face at $\frac{1}{32}$-inch intervals along the length of the piece at a location that would correspond as closely as

possible to the central axis of the original bar. Impressions at $\frac{1}{16}$-inch intervals on each of two parallel rows avoided overlapping between adjoining impressions. These hardness readings were then plotted versus the linear distance from the quenched end as shown in the accompanying curves. For lack of specific information on white cast iron, the cooling rate for steel as reported by Hill (8) is superimposed upon this chart to give a comparison of the probable cooling rate with the hardness attained in this piece of white cast iron.

A second quarter-section of this bar was polished and examined metallographically and typical microsections are shown in the accompanying top row of photomicrographs in Fig. 2. Their location with respect to the hardness and estimated cooling rate is indicated above each micrograph.

The remaining two quarter-sections were then treated as follows: A box of powdered graphite was heated to a temperature of 1680 degrees Fahr. (915 degrees Cent.) and the two sections were buried in the graphite at this temperature. One of the sections was removed from the box at the end of thirty minutes and given a water quench, while the other section was quenched after two hours at temperature. These sections were then heated to 600 degrees Fahr. (315 degrees Cent.) for one hour and again water-quenched to temper the martensite into a constituent which etched grayish-yellow. They were then polished and examined at $\times 100$ and $\times 500$ magnification. In the accompanying composite, Fig. 2, micrographs are shown which have corresponding cooling rates to correlate the as-prequenched structure with that obtained after a short first stage anneal.

To illustrate further the effect of severe and mild prequenching treatments upon the resultant structure after two hours of first stage anneal, additional photomicrographs at $\times 500$ are shown in Figs. 3A and 3B.

## Observations

By referring to Fig. 2, it is quite evident that numerous very fine graphite particles are obtained by annealing a prequenched white cast iron if the cooling rate has been sufficient to produce martensite. Such a cooling rate needs to be greater than 240 degrees Fahr. per second at 1300 degrees Fahr. (705 degrees Cent.) and results in a Rockwell hardness of 57 C or greater. Tiny spots of a very dark etching constitutent start to appear at a cooling rate of about 240

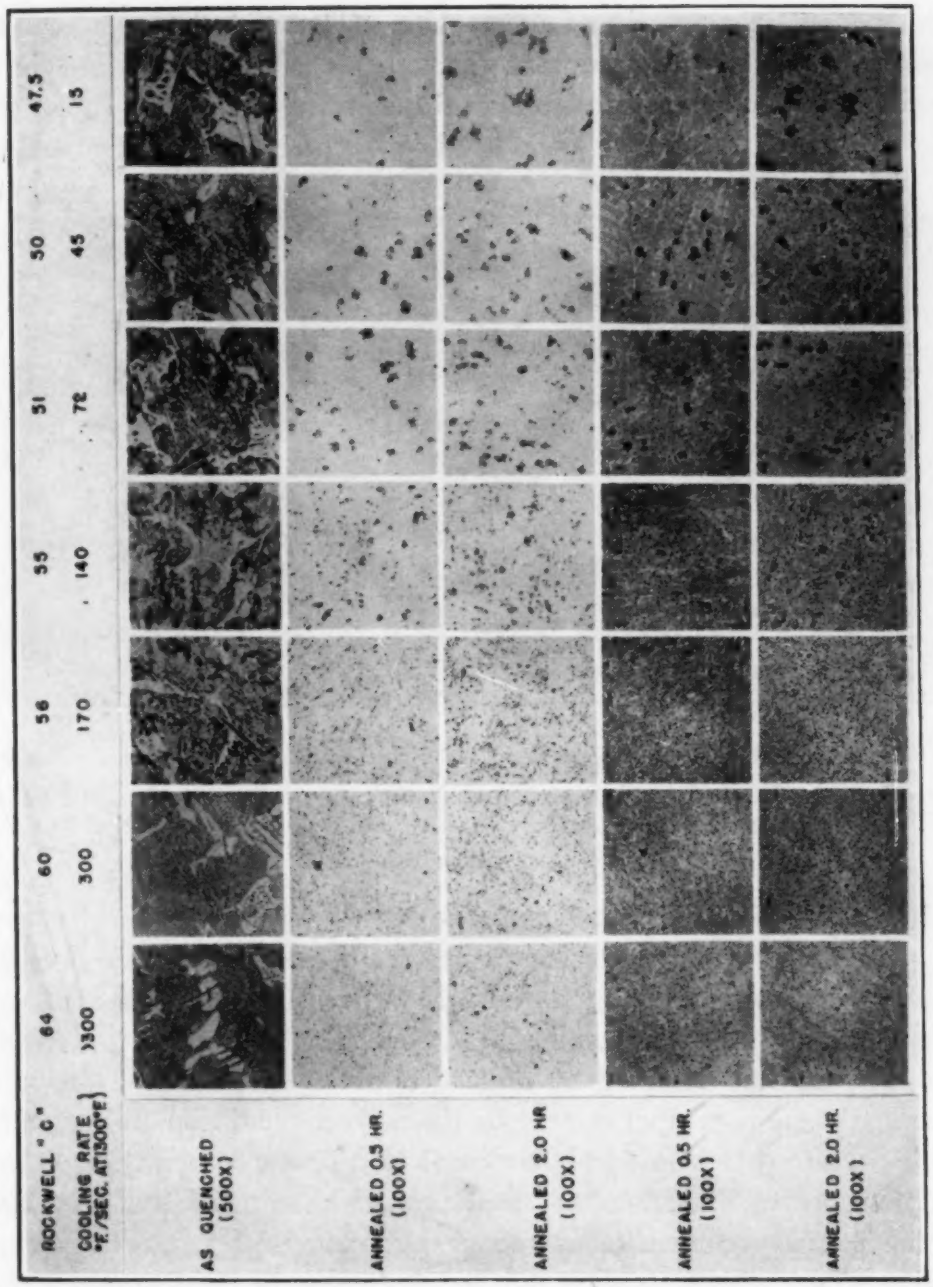
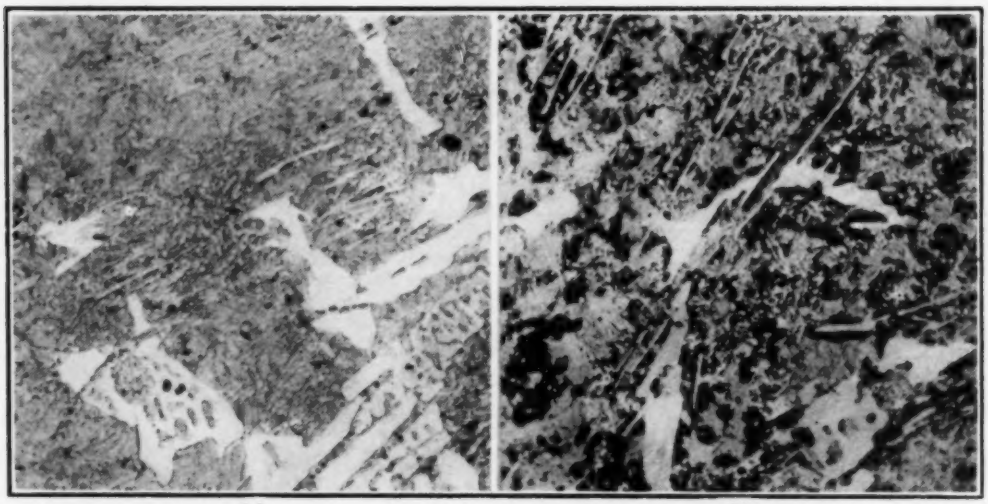



Fig. 2—Photomicrographs of the Cast Iron Specimen After the Treatment Noted. (Composite Reduced to One-Fourth in Reproduction).

Top or 1st row—Structures of the as-quenched white cast iron at points which have the rate of cooling and Rockwell C hardness noted at the top. 2nd and 3rd rows (Unetched), 4th and 5th rows (Etched 3 per cent Nital)—Graphite distribution and primary cementite residue after annealing the as-quenched structure of the top row for the time designated at the left.

degrees Fahr. per second and the amount of this constituent increases and the hardness decreases as the cooling rate becomes less. The micrograph at a rate of 170 degrees Fahr. per second and a Rockwell C of 56 shows many black spots which are quite well developed

interspersed in a matrix of martensite. These black spots are presumably fine pearlite (primary troostite) resulting from the intersection of the cooling rate curve with the nose of the "S" curve (9). The graphite resulting from this structure is slightly coarser



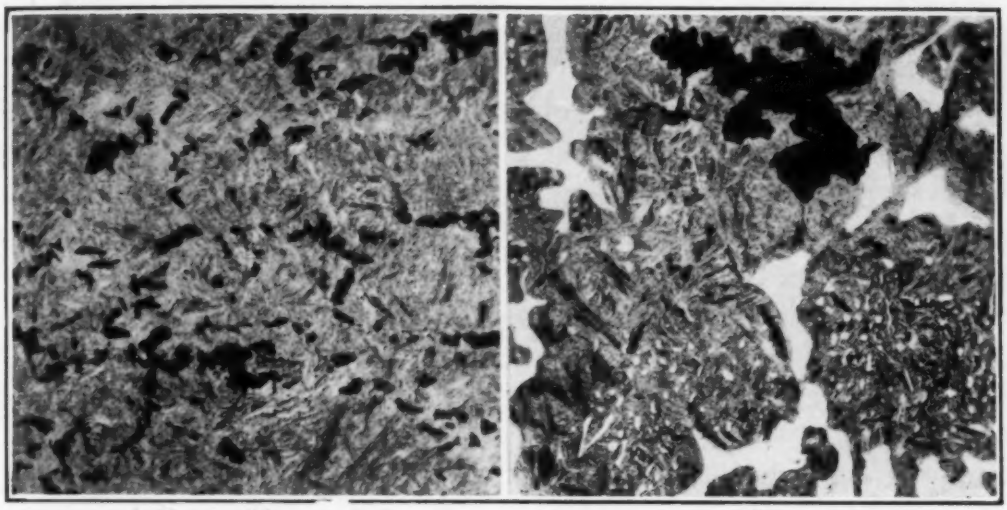
2A 2B

Fig. 2A and B—Detail of Two Micrographs from Fig. 2 Showing Structures of the As-quenched White Cast Iron, Nital Etch. × 500. Fig. 2A—300 Degrees Fahr. Per Second at 1300 Degrees Fahr., Rockwell C 60. Fig. 2B—170 Degrees Fahr. Per Second at 1300 Degrees Fahr., Rockwell C 56.

and less numerous than that obtained by a higher prequenching rate. At successively lower quenching rates the resultant graphite becomes gradually coarser until at a rate of 15 degrees Fahr. per second and a hardness of 47.5 Rockwell C, the resultant graphite is practically the same as that obtained by annealing an as-cast bar for the same time at the same temperature. In the as-cast condition the hardness of this white cast iron is 44 Rockwell C. The accompanying etched microstructures illustrate the decrease in the rate of disappearance of the primary cementite as the graphite nuclei become larger but fewer. Two hours is sufficient to complete the first stage anneal in the sections prequenched to martensite, but as the amount of martensite decreases the size of the graphite progressively increases and the amount of undecomposed primary cementite becomes progressively greater.

Fig. 3A shows the shape and distribution of the graphite obtained by a 2-hour anneal of the iron prequenched at a cooling rate of 300 degrees Fahr. per second at 1300 degrees Fahr. (705 degrees Cent.). The background or matrix is evidently free of all

cementite and is acicular as a result of having been quenched from the annealing temperature. The graphite exists in tiny flakes and slightly larger nodules distributed about the boundaries of the previous interdendritic cementite areas. Fig. 3B shows the equivalent



3A 3B

Fig. 3A and B—The Structures Obtained After Prequenching as Noted Followed by a 2-Hour Anneal at 1680 Degrees Fahr. Terminated by a Water Quench, Nital Etch. × 500. After 10 Minutes at 1634 Degrees Fahr., Prequenched at a Cooling Rate of: Fig. 3A—300 Degrees Fahr. Per Second at 1300 Degrees Fahr., and of Fig. 3B—15 Degrees Fahr. Per Second at 1300 Degrees Fahr.

result from a prequench of 15 degrees Fahr. per second at 1300 degrees Fahr. (705 degrees Cent.). Here the graphite exists in the form of widely separated large nodules in a matrix consisting of an acicular constituent containing much massive primary cementite and many well distributed spheroids of cementite.

## Discussion

The principle of the end-quench type of test for obtaining a graduated decrease in the severity of the quenching rate has been investigated repeatedly in connection with its ability to give results which are easily reproducible by different laboratories. The cooling rate attained by portions of the bar in this method of testing has been actually measured by Jominy (10), and Hill (8), and the cooling rate curves calculated to degrees Fahr. per second at 1300 degrees Fahr. (705 degrees Cent.) as reported by these two independent investigations are quite closely coincident. Also it has been reported by Hill (8) and Williams (11) that the cooling rates at corresponding points along the bar as attained by this method are practically independent of the diameter of the bar, the chemistry of the steel, or

the temperature of the quenching water, within wide limits of variation. For this reason it is assumed that the reported cooling rates apply to the white cast iron of the present instance and the curve of Hill is superimposed upon the accompanying chart of hardness versus location along the bar to provide definite information correlating the hardness and the cooling rate with the resulting modifications of graphite.

The accompanying photomicrographs of Fig. 2 show that if a white cast iron is prequenched to a martensitic structure, Rockwell C 56 or greater, many fine graphite nodules are produced during the first stage annealing treatment. As the prequench structure becomes progressively less martensitic and softer, the resultant graphite becomes coarser and more widely separated. At the higher magnification of Fig. 3A the graphite exists in tiny flakes and nodules outlining the previous interdendritic cementite areas. It is possible this results because the nuclei formed in great numbers at the austenite-cementite interface and grew as the cementite disappeared; thus, the collective effect was that they outlined the dendritic areas. The occasional nodules which appear to exist at some distance from any primary cementite probably arise from nuclei at some primary cementite-austenite interface existing in a plane not visible in the micrograph because of the third-dimensional factor present in a solid material. The more drastic quench results indirectly in fine graphite for the direct result is the formation of nuclei in such great numbers that their subsequent growth exhausts all of the available massive cementite before any of them have been able to grow to any appreciable size. These nuclei are very numerous so the surface area available for the deposition of carbon from the dissociation of the dissolved carbide is correspondingly great.

When the nuclei are very limited in number, the dissociation is correspondingly hindered. Thus, in Fig. 3B the graphite exists as widely separated large nodules in a matrix containing much massive cementite and many well distributed spheroids of cementite. Possibly these spheroids are formed in the following manner: At the first stage annealing temperature considerable more carbon[2] is soluble than is the case at the critical temperature. Therefore, as the temperature drops, this carbon is precipitated from the now supersaturated solid solution upon cementite nuclei which grow in

[2]The term dissolved carbon, in the sense that it is used here, is understood to refer to combined carbon in solution.

all directions to an approximately spherical form. These nuclei may be newly formed or they may be undissolved remnants of the pearlite phase. As the cementite spheroid forms, carbon diffuses from the remaining austenite which is thus lowered in carbon content to an amount that will change bodily to martensite without further precipitation.

In the specimens having fairly coarse graphite, there is an area immediately surrounding the graphite nodule which appears to be free of spheroids. The cause of this is uncertain but may be as follows: The solubility of carbon in equilibrium with graphite is less than the solubility of carbon in equilibrium with cementite at the same temperature above the critical. The austenite surrounding graphite will be in equilibrium with that graphite while the austenite surrounding cementite will be in equilibrium with that cementite. However, since these equilibrium concentrations are at different levels there is of necessity a flow of carbon from the regions of higher concentration surrounding the cementite to the regions of lower concentration surrounding the graphite. Therefore, to reach equilibrium, cementite will go into its solution and graphite will grow from its solution. Now when the specimen is rapidly cooled the portion immediately in the vicinity of the graphite contains only a small supersaturation of carbon and this readily diffuses to and dissociates upon the graphite while the greater concentration present in the vicinity of the cementite forms a great supersaturation of carbon and this diffuses only to the extent of forming spheroids of cementite practically in situ. When the massive cementite has become exhausted the remaining austenite rapidly reaches the lower carbon content in equilibrium with the graphite and thus there is no precipitate of cementite spheroids present in the specimens where the massive cementite has been absorbed.

## Summary

1. A study of the effect of the rate of prequenching a white cast iron upon its subsequent graphitization behavior has been made on an iron of the following approximate analysis: Total carbon = 2.50, silicon = 1.30, manganese = 0.45, phosphorus = 0.082, and chromium = less than 0.018.

2. When the iron was prequenched at a rate of over 240 degrees Fahr. per second at 1300 degrees Fahr. (705 degrees Cent.) to a Rockwell hardness of 57 C or greater, subsequent annealing at

1680 degrees Fahr. (915 degrees Cent.) gave very numerous and very fine graphite nodules outlining the interdendritic cementite areas.

3. Slower quenching rates to lower hardness values yielded progressively fewer and coarser graphite nodules on annealing.

4. The number of graphite nuclei formed appears to determine the rate of the subsequent graphitization reaction by its effect upon the surface area available for deposition of carbon from the dissociation of the dissolved carbide.

ACKNOWLEDGMENT

The author wishes to express his appreciation for the support of Battelle Memorial Institute in the work reported here and for the helpful suggestions of Dr. C. H. Lorig and for the assistance of other associates at the Institute.

The iron used was furnished by The Albion Malleable Iron Company through the intercession of Professor R. Schneidewind of the University of Michigan to whom grateful acknowledgment is also extended.

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## DISCUSSION

**Written Discussion:** By H. A. Schwartz, manager of research, National Malleable and Steel Castings Co., Cleveland.

The contribution which Simmons has made to the problem he investigated is the substitution of certain quantitative ideas of cooling rates for the qualitative information previously obtained. His work appears to confirm that of Hultgren, who came to the conclusion that prequenching accelerated graphitization only if it formed martensite.

Simmons' adaptation of the Jominy quench to this problem is a very ingenious contribution to the technique of investigating the phenomenon. His observations have omitted any consideration of a variable maximum temperature. It was rather evident in the experimentation associated with the quotations which Simmons makes from this writer that the prequenching acceleration of anneal was decidedly more marked if quenching were from 1000 degrees Cent. (1830 degrees Fahr.) than if it were from 900 degrees Cent. (1650 degrees Fahr.). This statement is made with the implication that castings of a given size are under consideration.

One expedient has been used in the paper which has caused this commentator some confusion. Apparently Simmons has referred to cooling rates at 1300 degrees Fahr. (705 degrees Cent.) as an arbitrary and convenient means of expressing the entire cooling cycle at any given section. In conjunction with Hill's data one could, of course, refer to Simmons' observation of the cooling rate at any other temperature.

The writer would be glad to know whether a selection of 1300 degrees Fahr. (705 degrees Cent.) had any particular purpose; that is, whether the author believes that the cooling rate in this temperature range is more closely correlated with the results than the cooling rate measured at some other temperature. It would seem that, as a matter of fact, a cooling rate nearer to the nose of the S-curve might have more actual meaning. The explanation offered in the paper for the finer distribution of temper carbon, and the acceleration of graphitization caused thereby, seems to be in entire harmony with the knowledge which this laboratory possesses with regard to the problem.

**Written Discussion:** By W. D. McMillan, chief chemist and metallurgist, International Harvester Co., Chicago.

This paper makes reference (7) to an article by A. Hultgren and O. Edstrom which was unavailable to the author. We have had occasion to review a patent issued in the name of Axel Hultgren, United States Patent No. 2,185,894 which pertains to the development of graphite nuclei by quenching white cast iron. The Hultgren article to which the author makes reference was published in 1942. The application for patent, presumably by the same author, was made in January, 1937. However, information contained in the write-up of the patent may be of interest and is summarized briefly as follows:

> On malleableizing at 1700 degrees Fahr. graphite particles formed, without prequenching, were 75-100 per square millimeter.
>
> On quenching from 1790 degrees Fahr. followed by rapid heating and malleableizing at 1790 degrees Fahr. the count was about 14,000 per square millimeter.

These results were obtained on 6-millimeter rods containing 3.0 per cent carbon and 0.95 per cent silicon and quenched in oil under which conditions the bars were martensitic. It was found that when larger castings were quenched in oil the matrix becomes sorbitic and the graphite particles subsequently formed are not increased in number as they were when the matrix was martensitic. When larger castings are quenched in water, cracks develop which cannot be avoided.

On the basis that a martensitic matrix is necessary to increase the number of graphite nuclei by prequenching, nickel, chromium, molybdenum and higher manganese have been used to increase the hardenability so that heavier castings will become martensitic when quenched in oil.

Mr. Simmons has found that when the prequenching rate is sufficient to produce 57 Rockwell "C" or greater and the structure is largely martensitic, many fine graphite nodules are produced in annealing. Also, that when a structure becomes progressively less martensitic and softer the resultant graphite becomes coarser and more widely separated.

The author has given a very interesting picture of this effect on the graphite count and has sufficient data to establish a rate from a hardness of 64 down to 47.5 Rockwell C. While it is quite possible that Mr. Hultgren likewise had considerable data the information disclosed in his patent description is that when the iron is sorbitic from the quench and probably on the order of 45 Rockwell C no increase in the number of graphite nuclei results from a quench prior to annealing and when the structure is martensitic a marked increase in count obtains.

Mr. Simmons comments that the number of graphite nuclei formed appears to determine the rate of the subsequent graphitization reaction by its effect upon the surface area available. A higher number of graphite nuclei and a uniform distribution definitely shorten the time required for complete graphitization not only due to surface area but because the distance between nuclei is shorter.

There are several other factors which have come to our observation that have an effect on the number of graphite nuclei. Iron with a silicon content of about 1.0 per cent has been observed to have a count of from 6 to 20 depending upon the annealing cycle. An iron of a higher silicon content, 1.60 per cent, will normally have a count of 30 to 50, that is, there is a tendency for greater number of nuclei as the silicon content is increased.

It has been observed that metal which has been oxidized excessively in melting will exhibit a much lower graphite count than iron of the same silicon content melted down normally.

It has been found that iron removed from the furnace at the completion of the first stage of graphitization will exhibit a considerably higher count than when the iron has been allowed to remain at the maximum annealing temperature after the first stage is complete. Briefly, when castings are soaked longer than necessary, the graphite count is decreased and the second stage of annealing is to some extent retarded.

Again, when hard iron castings are heated for a few hours at a temperature between 500 and 1000 degrees Fahr. this practice is effective in increasing the number of graphite nuclei. When the subsequent annealing cycle is adjusted to take advantage of this the total time required to obtain a fully ferritic structure is considerably less.

While these comments may not pertain directly to the prequenching of white cast iron to which subject Mr. Simmons has made an interesting contribution, the purpose of prequenching is to increase the graphite count in the interests of shortening the annealing time. For this reason we have mentioned other factors affecting the graphite count.

**Written Discussion:** By Charles H. Junge, Armour Research Foundation, Chicago.

This study of the effect of prequenching treatment before graphitization of a white iron indicates rather definitely that the phenomenon of fine temper carbon formation is related not to changes occurring in the massive carbide phase, as has been alleged by previous investigators, but rather to changes operative in the matrix portion of the alloy. Additional evidence that this is so is furnished by the behavior of certain graphitizable steels that may have a composition of about 1.30 per cent carbon and 1.60 per cent silicon. When molten steel of this composition is poured into water, the resulting shot when examined microscopically shows no carbide but only extremely coarse martensite and some retained austenite. If such quenched material is now subjected to a graphitizing treatment below $Ac_1$, rather striking pseudomorphs of the coarse martensite needles are produced by the resulting fine flake-like graphite particles. This reproduction of the acicular structure of the parent martensite is less distinctly visible, yet clearly recognizable, if graphitization is conducted above the $Ac_1$ temperature.

White iron shot quenched from the liquid state will behave in a somewhat similar manner when graphitized at temperatures below and above $Ac_1$, but the effect is not so striking, perhaps because the martensite needles are not as large in such material, since their growth has been obstructed by the massive carbide phase dispersed throughout the matrix. However, the case of the graphitizable steels, where massive carbide is never present, would seem to tie the fine temper carbon precipitation rather convincingly to the condition of the matrix. Incidentally, the degree of supersaturation of carbon in the martensite made possible by quenching *liquid* white iron or graphitizable steel is much greater than can be realized by quenching such materials from temperatures in the vicinity of 900 degrees Cent. (1650 degrees Fahr.).

That spheroidized cementite resulting from the tempering of quenched steels will produce pseudomorphs of the parent martensite is well known. Whether the mechanism operative in the graphitizable materials is (1) the production of the spheroidized cementite pseudomorph, then (2) the graphitization of such carbide particles; or whether the graphite nuclei form directly from the martensite, is subject to speculation. The present writer feels that the tremendous surface area presented by the multitude of fine cementite particles which would be produced upon heating the martensite may have considerable influence in bringing about the fine temper carbon structure, since it has been suggested by several other investigators that the interface between carbide and matrix is a preferred location for graphite nucleation. That this matrix need not be austenite is amply demonstrated by the graphitizing experiments conducted below $Ac_1$.

### Oral Discussion

CHARLES WALTON:[3] A possible reason for the increased number of graph-

[3]Metallurgist, Association of Manufacturers of Chilled Car Wheels, Chicago.

itization nuclei has occurred to me during the presentation of the paper. It is known that in drawing martensite a very fine dispersion of carbides is obtained. These carbides in the presence of enough silicon may decompose and thus form a large number of graphite nuclei.

**Author's Reply**

Mr. McMillan referred to a U. S. Patent issued to Hultgren pertaining to this prequenching operation. The introduction of alloys to increase hardenability is perfectly feasible, but the effect of the alloys upon graphitization must be considered. For instance, aluminum would increase the hardenability, but might also produce primary graphitization, or manganese would very greatly inhibit second stage graphitization though the first stage would not be affected to any noticeable extent.

The number of graphite nuclei and their uniform distribution shortens the time if they are present in great numbers. However, the internuclear distance is considered to be of minor importance. For instance, if a completely malleableized iron is reheated to above the critical temperature, less than a minute is necessary to completely saturate the austenitic matrix with carbon; thus it is likely that the diffusion time would be a minor factor.

The decrease in number of graphite particles at the first stage with prolonged heating occurred in one set of prequenched specimens whereas in all other sets no change took place, that is, the number of nodules appeared to remain constant, and it was assumed that perhaps the medium in which the material was annealed may have been responsible.

Samuels and Lorig found that baking iron at a temperature of around 600 degrees Fahr. (315 degrees Cent.) very greatly accelerated the amount of graphitization that later took place above the critical and gave the finer type of graphite nodules. However, it is very likely that this mechanism of reaction at around 600 degrees Fahr. is different from that above the critical range.

Dr. Schwartz mentioned that the temperature of prequench had a very great effect. I assume that the greater solubility of cementite in austenite at the higher temperature would yield a greater number of nuclei upon quenching.

The temperature of 1300 degrees Fahr. (705 degrees Cent.) was chosen arbitrarily to indicate the cooling rate because of the several curves for that temperature in the literature. Some temperature from the "S" curve might have more significance, but if this should be taken to be at the nose, the cooling rate of Hill would pertain only to the austenite that had not transformed as the transformation product would be likely to have a different cooling rate.

Mr. Junge gave very interesting information on graphitizable steels having carbon sufficiently low to avoid massive cementite. In cast iron, quenching from the molten state will produce a much greater supersaturation of cementite in solid solution than may be obtained by quenching from temperatures around 1700 degrees Fahr. (925 degrees Cent.), but only 1.3 per cent carbon will dissolve in this graphitizable steel regardless of the temperature. I have noticed on some work done with quenching molten white cast iron where very large grains of austenite surrounded by cementite were obtained that upon annealing for five minutes at 1500 degrees Fahr. (815 degrees Cent.) there was a very marked precipitation of fine cementite nodules from the martensite needles produced by

the primary quench. Upon annealing for fifteen minutes at 1500 degrees Fahr. (815 degrees Cent.), complete graphitization had taken place, but the graphite that formed outlined the boundaries of the previous massive cementite and the dendritic austenite. There seemed to be very little graphite precipitated in the austenitic-dendritic matrix, which led to the conclusion that any graphite that existed there originally formed at a massive cementite-austenite interface existing below the surface where it could not be seen because of the third dimension factor. Thus, it was considered that this precipitate of secondary spheroids of cementite was of only minor importance as a source of nuclei.

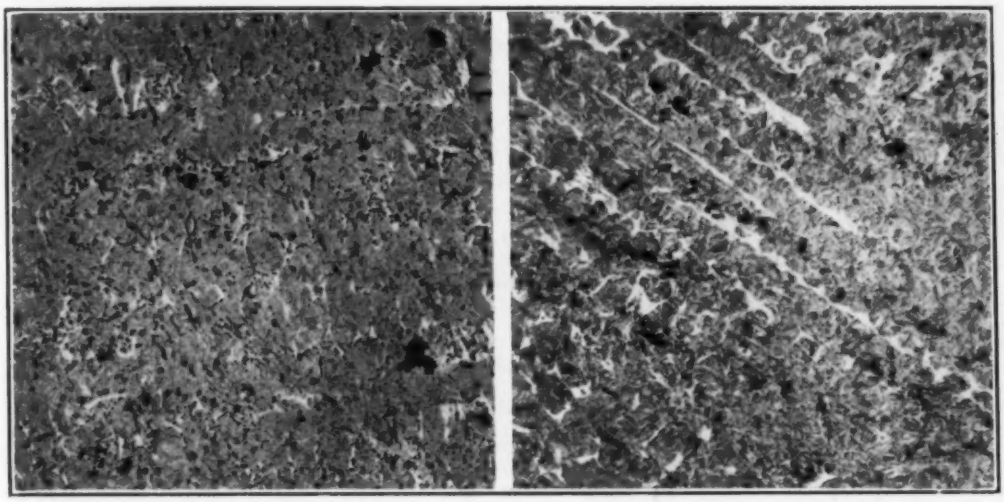

Fig. A Fig. B

Figs. A and B—The Structures Obtained After Prequenching at a Cooling Rate of 300 Degrees Fahr. Per Second at 1300 Degrees Fahr. From 10 Minutes at 1634 Degrees Fahr., Followed by a One-Half Hour Anneal at 1680 Degrees Fahr., Terminated by a Water Quench. Nital Etch. × 100. Fig. A—T.C. = 2.50, Si = 1.30, Mn = 0.45, P = 0.082. Fig. B—T.C. = 2.50, Si = 0.96, Mn = 0.35, P = 0.10.

Mr. Walton's statement that a possible reason for the increased number of nuclei may be the decrease in stability of cementite produced by the high silicon content of these irons was anticipated, so an iron of about standard composition, total carbon = 2.50 and silicon = 0.96, was treated simultaneously and in the same manner as the iron reported. In the region of the rapid prequench and high hardness a one-half hour anneal was sufficient to practically eliminate the massive cementite in the iron where the silicon was 1.30 per cent whereas considerable massive cementite was still present in the iron which contained only 0.96 per cent silicon, as shown in Figs. A and B, respectively. The main effect of the silicon evidently is to increase the rate of decomposition of the cementite and make the effect of the prequench more marked, for very fine graphite is present in both micrographs.

I appreciate very greatly the interest that has been taken in this paper.

# PSEUDOMORPHS OF PEARLITE IN QUENCHED STEEL

By Owen W. Ellis

*Abstract*

*In this paper further evidence is provided of the rapidity with which steel can be raised above the critical range by induction heating. It is shown that the point is almost reached where steel, after induction heating, can be quenched before any change has occurred in it, other than that from alpha iron to gamma iron. On this account, it is possible to obtain by rapid induction heating and immediate quenching pseudomorphs of structures purposely formed in steel before heating and quenching. It is suggested that such pseudomorphic structures may have properties worthy of fuller study and of application in engineering and that in the future, on this account, less stress should be placed on ensuring that diffusion occurs during induction heating.*

INDUCTION heating provides the engineer with means for raising the temperature of steel so rapidly that the point is almost reached where the steel, after heating, can be quenched before any change has occurred in it, other than that of alpha iron to gamma iron. The foregoing statement covers grain size as well. From a theoretical point of view, heating of steel from room temperature could be so rapid and quenching so immediate as to prohibit diffusion, with the result that a perfect pseudomorph of the original structure of the steel would be obtained after quenching it from above the critical range. For example, one can imagine steel having a spheroidized structure being heated above the critical range so rapidly and being quenched so immediately that, even though the ferrite momentarily changed to austenite of the same composition as the ferrite, the quenched structure would be identical with the original structure of the steel. Presumably the physical and mechanical properties of the quenched steel would differ from those of the spheroidized steel only to the extent that the ferrite between the carbide spheroids was altered by heating above the critical range and rapid quenching. If one were dealing with a straight carbon steel,

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the difference between the properties of the quenched steel and the original steel might be small; however, if one were dealing with an alloy steel, the ferrite of which held much alloy in solution, quenching might be quite important in its effect on the physical and mechanical properties of the quenched steel, despite the fact that the carbide spheroids remained quite unaffected during heat treatment.

In practice, however, the rate of diffusion of carbon in gamma iron is so high—the rate being higher the higher the temperature—that it is impossible to prevent some transfer of carbide from the spheroids to the surrounding austenite, with some consequent loss of identity of the spheroids. Hence the quenched structure of induction-heated spheroidized steel will differ somewhat from that of the untreated steel. Time will, of course, be an important factor in determining the extent of the structural change.

To check the extent to which the structure of spheroidized steel would be altered by rapid heating to and immediate quenching from a temperature above the critical range, use was made, through the courtesy of Thompson Products Limited, St. Catharines, Ontario, of a Tocco unit designed for the hardening of armor piercing shot. The coil in this unit was so arranged that, at a point approximately 4.5 inches from the base of a shot, a temperature of 1565 to 1585 degrees Fahr. (850 to 865 degrees Cent.) was reached in 130 seconds after power had been applied to the coil. In these experiments the shot were quenched 30 seconds after they had reached their maximum temperature. In all probability, temperature gradients existed in the shot at the time of quenching. However, a sample cut from the nose of the shot, exposing a transverse section approximately 0.25 inch from the point of the shot, and a sample cut from the outside of the body of the shot, at a point 3.25 inches above the base of the shot, showed structures which were somewhat similar in appearance (see Figs. 2 and 3). It may be assumed, therefore, that these structures, and others to which we refer below, were obtained as a result of quenching rapidly-heated steel from temperatures not much below 1565 to 1585 degrees Fahr. It may well be observed that, despite the variations in temperature which existed in the shot at the time of quenching, carbide spheroids existed therein throughout.

The question may be asked "Why were you interested in determining the extent to which the structure of spheroidized steel would be altered by rapid heating to and immediate quenching from

a temperature above the critical range?" We were interested in this because, in many instances, what appeared to be pseudomorphs of pearlite were observed throughout shot which had been subjected to the treatment referred to in the previous paragraph, the steel having beforehand been given a pearlitic structure as a result of isothermal annealing at 1225 degrees Fahr. (660 degrees Cent.). It was believed that these pseudomorphs were nothing but the slightly changed structures of the untreated steel. If, in such steel, as a result of rapid heating and immediate quenching, a pseudomorph of

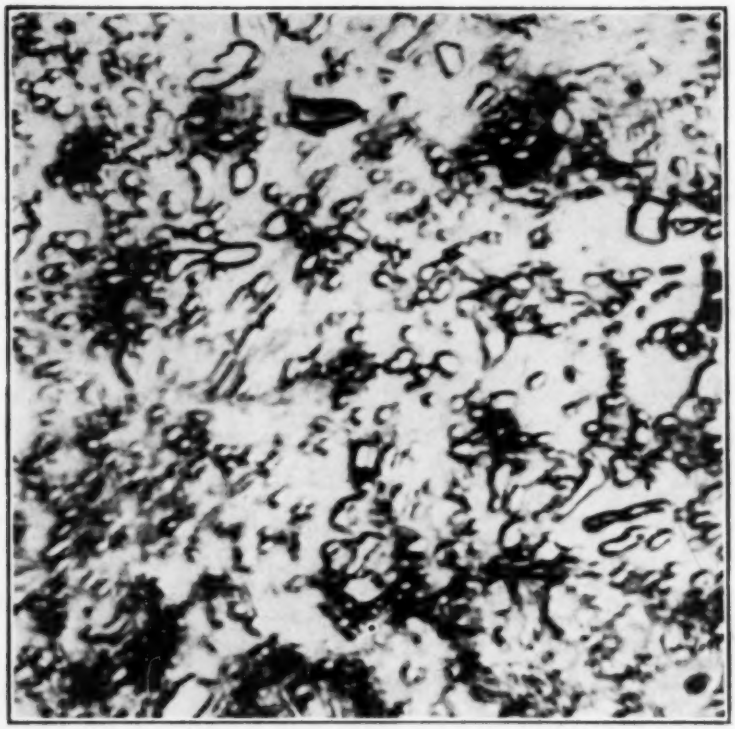

Fig. 1—Structure of Spheroidized Steel Before Induction Treatment. × 2000.

pearlite could be obtained, then, it was argued, by the same means a pseudomorph containing spheroidized carbide should be produced in steel which had been previously spheroidized.

Pseudomorphs of pearlite have been observed in quenched steels by many workers. Bain, in his book "Functions of the Alloying Elements in Steel", has remarked "It has been shown that the solution of carbide is a time-consuming operation; even though it is rapid in pure iron-carbon alloys it is slow in some alloy steels. This is because diffusion is time-consuming and only through diffusion

may austenite be rendered homogeneous, for the austenite formed at the former location of carbide particles is very rich in carbon. The author has seen quenched steels which had been heated for hardening from a coarsely pearlitic state in which the markings of the original lamella were clearly visible in the microscopic specimen of resulting martensite. The reason the etching reagent may reveal the pattern is that the martensite was of uneven carbon content; low in the former ferrite lamellae zones, high in the cementite lamellae locations." This clearly describes the conditions requisite for the retention of the pseudomorph of pearlite in what may be described as relatively sluggish steels. However, the rate of heating of these steels was probably, if not undoubtedly, slow; certainly far slower than that used in the experiments described above. The further point may be made that the pearlitic pseudomorphs now under discussion were found *all through* the shot dealt with as described above.

Steel of the following nominal analysis was used in these experiments:

| | |
|---|---|
| Carbon | 0.61-0.65 |
| Silicon | 0.28-0.33 |
| Manganese | 0.75-0.90 |
| Sulphur | 0.025 max. |
| Phosphorus | 0.025 max. |
| Chromium | 0.65-0.85 |
| Molybdenum | 0.30-0.35 |
| Nickel | 0.70-0.90 |

Fig. 1, at a magnification of 2000 diameters, shows the structure of the untreated spheroidized steel to which we have already referred. The divorce of pearlite, because the steel had a pearlitic structure (see Fig. 4) to begin with, was brought about by annealing it at 1300 degrees Fahr. (705 degrees Cent.) for 72 hours. Figs. 2 and 3, both at a magnification of 2000 diameters, show the structures in the same steel after it had been heated to 1565 to 1585 degrees Fahr. (850 to 865 degrees Cent.) in 130 seconds and vigorously quenched 30 seconds later. Here, in a matrix of martensite, can be seen a few spheroids of carbide. These are some of those which have retained their identity despite the fact that they may have been reduced in size as a result of partial solution in gamma iron. Most of the smaller spheroids and most, if not all, of the lamellae which characterized the steel in its original state (Fig. 1) have disappeared; sufficient of the spheroids remain, however, to support the view that more rapid heating and more immediate quenching would have resulted in fewer spheroids and lamellae being dissolved during their stay above the critical range. Fig. 2 shows the structure of the steel

near the surface of the shot at 3.25 inches above the base: Fig. 3 that of the steel near the nose of the shot. In passing, it may be remarked that the reaction to etching of the two samples—the one from the side and the other from the nose—was quite different. It was found very difficult to etch the sample from the nose so as to bring out the spheroids clearly in the photograph, though they could be readily distinguished under the microscope.

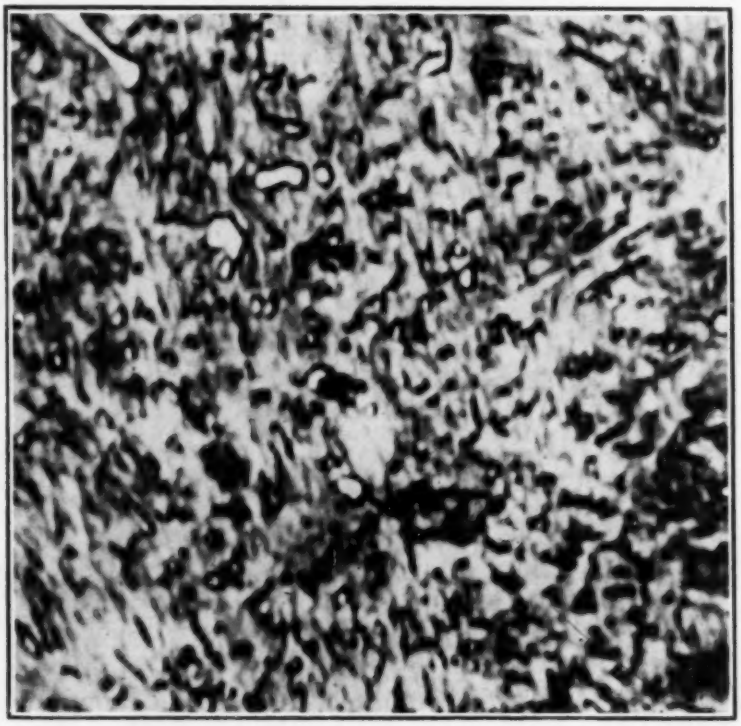

Fig. 2—Structure of Induction Heated and Hardened Spheroidized Steel. Side of Shot. × 2000.

The hardness of the steel in the original spheroidized state varied from Rockwell "B" number 102 to Rockwell "B" number 107. The Vickers hardness of the steel after quenching was in the immediate neighborhood of 750; the Rockwell "C" hardness number varied between 62 and 63. The hardness was the same in both the sample from the nose and the sample from the body of the shot. These results suggest that, while it is possible to heat steel so quickly and to quench it so rapidly from above the critical range, sufficient diffusion of carbon into the gamma iron lattice occurs to enable martensite to be obtained on quenching. It is possible that the concentration gradients in the austenite, and in the martensite resulting

from its rapid cooling, are quite high, the iron lattice immediately adjacent to the spheroids being supersaturated with carbon and that distant from the spheroids being relatively free from carbon. Etching, however, does not suggest that heterogeneity exists in the martensite. It is not entirely impossible that at points very remote from the spheroids the iron lattice will contain no more carbon than did the original ferrite of the untreated steel. We have not considered the effects of other elements upon the behavior of the steel under the

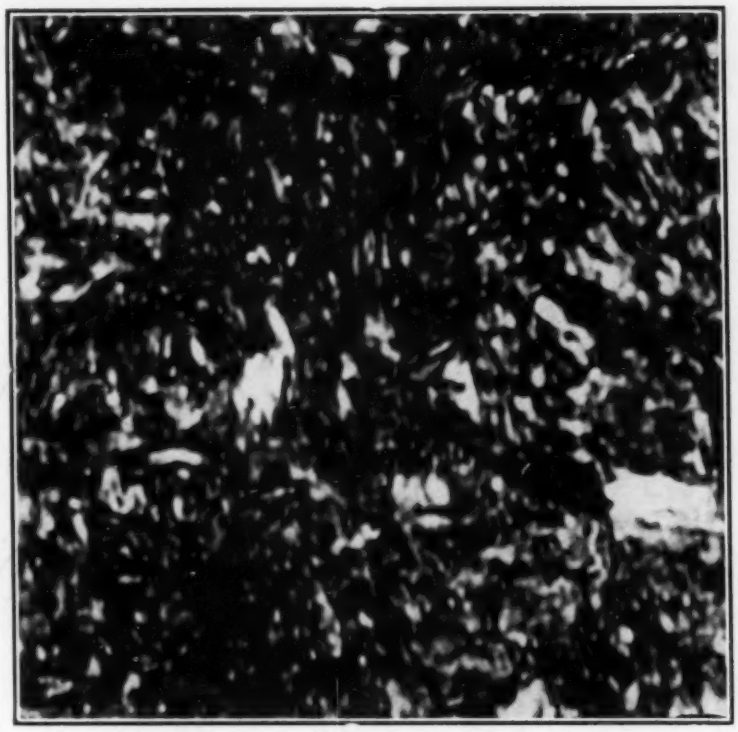

Fig. 3—Structure of Induction Heated and Hardened Spheroidized Steel. Nose of Shot. × 2000.

above conditions, but are not overlooking the fact that elements, such as chromium in particular, will have an important influence in this connection (1), (2), (3), (4).*

To turn now to the pseudomorphic pearlite which was the cause of the above investigation of spheroidized steel; in Fig. 4, at a magnification of 750 diameters, is shown the pearlitic structure which characterizes this steel after it has been fully annealed isothermally at 1225 degrees Fahr. (660 degrees Cent.). If the steel, having this structure, be treated as already described, it will, after quenching, as often as not, have a structure similar to that shown in Fig. 5 (at a magnification of 750 diameters). This can readily be mis-

*The figures appearing in parentheses refer to the bibliography appended to this paper.

taken for pearlite; in fact, the author himself refused to accept the evidence of this photomicrograph until he had proved by test that the hardness number of the steel was in the neighborhood of Rockwell "C" 62.5. At first he thought that, due to a defect in the equipment, the steel had not been heated above the critical range before quenching.

The conditions requisite for the production of the pseudomorph of pearlite are somewhat critical. In the first place, the steel must have a well-defined pearlitic structure to start with; this need not,

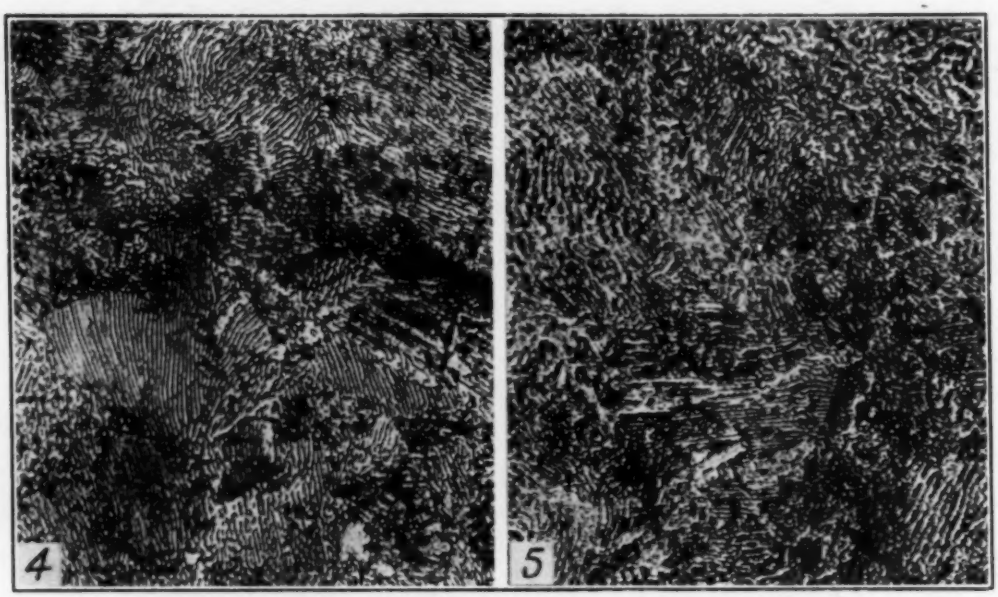


Fig. 4—Structure of Lamellar Pearlite in Steel Before Heating and Quenching in Tocco Machine. × 750.
Fig. 5—Structure of Pseudomorph of Pearlite in Steel After Heating and Quenching in Tocco Machine. × 750.

however, be obtained by isothermal annealing. In the second place, the power input has to be just such as to raise the temperature of the steel to the right point in the right time; the power input determines both the rate of heating and the maximum temperature of the steel and, therefore, the time that the steel is above the critical range before quenching. The time that the steel is above the critical range before quenching is of considerable importance, the maximum temperature attained by the steel is, caeteris paribus, of equal, if not greater, importance. If either of these factors be increased the steel loses its pseudomorphic structure and may exhibit, on quenching, the structure which has been described by Benninghoff as vermiform martensite. This structure is shown in Fig. 6, at a magnification of

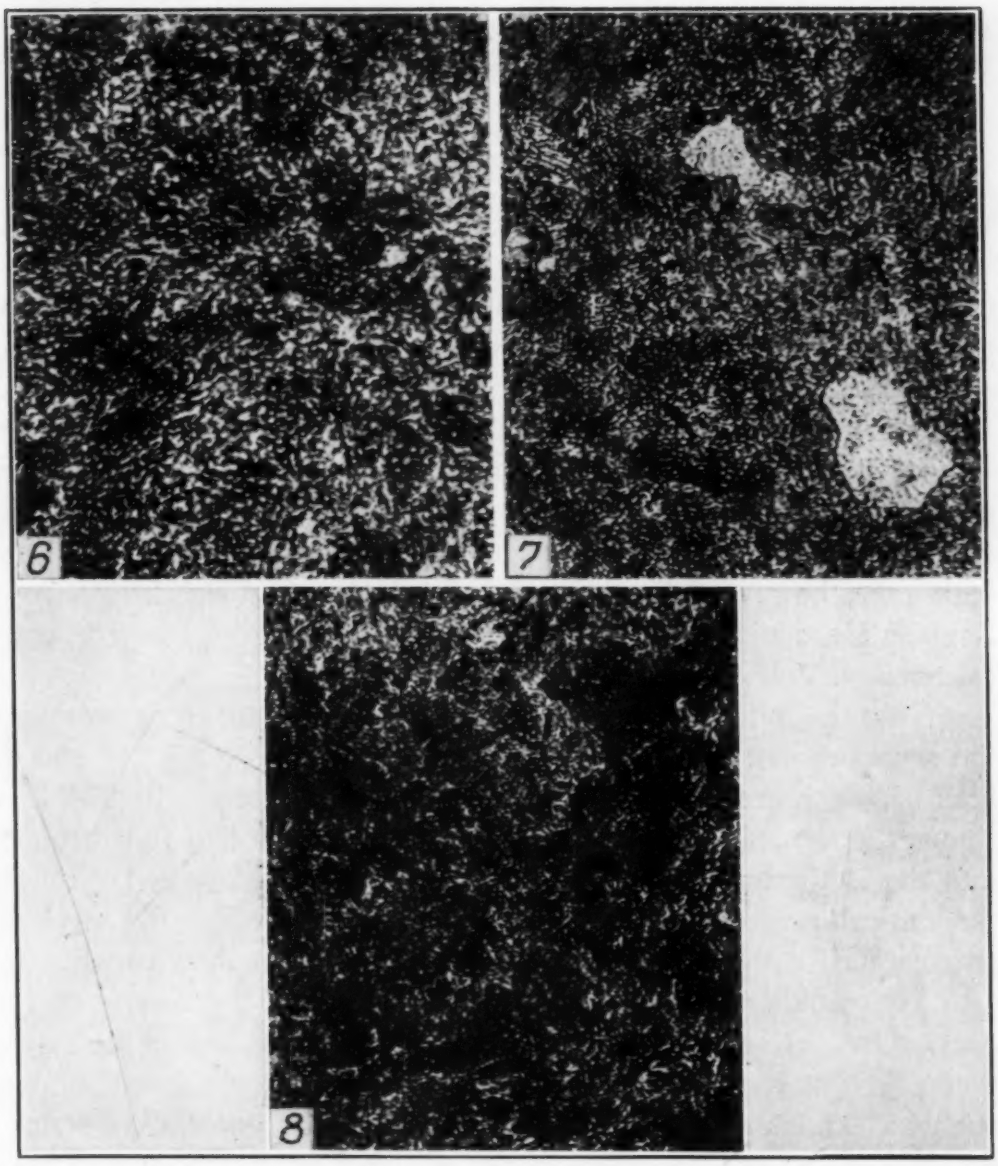


Fig. 6—Structure Resulting from Holding Steel in Tocco Machine Above Critical Range Long Enough Before Quenching to Allow Some Diffusion of Carbon to Occur. Vermiform Martensite! × 750.

Fig. 7—Pearlite in Steel Before Heating and Quenching in Tocco Machine. To Be Compared with Structure Shown in Fig. 8. × 750.

Fig. 8—Structure of Steel, Whose Original Structure Was That Shown in Fig. 7, After Treatment in Tocco Machine. × 750.

750 diameters. It may well be compared with that shown in Fig. 5. The comparison will be suggestive of how the pseudomorph loses its identity if either the time or temperature of heating above the critical range is prolonged.

It will be obvious that the concentration gradient of carbon in the iron lattice between the lamellae of carbide in the pseudomorph

of pearlite may be very high, whatever the form of the lattice. In the martensite resulting from rapid cooling the lattice will be supersaturated with carbon in the immediate vicinity of the carbide lamellae, but will be relatively free from carbon on lines midway between the carbide lamellae. Presumably the concentration gradient of carbon in the austenite, or, when quenched, martensite lamellae of the vermiform material, which seems to represent one of the first steps towards equilibrium in the steel above the critical range, is less than that in the clearly-defined pseudomorph which can result from ideal conditions of heating, holding and quenching.

The possibility that the pearlitic pattern may be developed by etching because the martensite, to use Bain's words, is "of uneven carbon content" cannot be discounted, but the fact remains that the chances that carbide can be retained in certain alloy steels is very high (see, however, discussion by Osborn on carbide diffusion — Surface Hardening by Induction, *Transactions* of the Electrochemical Society, Vol. 79, 1941, p. 1).

That the initial structure of the steel is important in determining the structure of the steel after treatment is shown in Figs. 7 and 8, both of which are at a magnification of 750 diameters. In Fig. 7 is shown the structure of a sample of this steel which had failed to get into the isothermal annealing furnace before it had passed through the critical range on cooling. The result of treating the steel in strict accord with the schedule already described is shown in Fig. 8.

The rapidity with which steel can be heated by means of induction has, of course, been recognized before. Tran and Benninghoff (5), who have done the pioneer work in this field, have pointed out that "To completely insure the success of the process" of induction hardening "the steel used should be either previously heat treated to a predominantly sorbitic structure or normalized to obtain a grain size that approaches the heat treated structure. This structure may be obtained by an accelerated cool from the normalizing temperature. The heating cycle in this process is so rapid that it permits little or no diffusion time, which necessitates having the steel in the proper condition before hardening." To illustrate this point Tran and Benninghoff show photomicrographs of "S.A.E. 1050 steel as forged and induction hardened showing incomplete dispersion of carbides due to too rapid heating not allowing sufficient time for complete carbide diffusion. Another ½ second was sufficient for complete diffusion".

The question of carbide diffusion during induction heating has also been dealt with by Tran and Osborn (6) who state that "The usual acicular martensitic structure resulting from furnace hardening is definitely absent" in steel hardened inductively under what may be termed commercial conditions. Instead "a more homogeneous structure, a nodular type martensite of obviously greater fineness" is formed. This nodular martensite is presumably akin to vermiform martensite in its nature. The former probably results from the transformation of lamellar pearlite, the latter from the transformation of sorbitic pearlite.

It is only natural that, if steel having a structure of tempered martensite or of bainite be heated above and cooled below the critical range with sufficient speed, the structure of the quenched steel will approach closely to that with which we are familiar in orthodox heat treatment; but where the steel is built up of widely separated (speaking relatively, of course) masses of carbide in a matrix of ferrite, the concepts of the behavior of the steel on hardening, based on equilibrium conditions, must go by the board when induction-hardening is under consideration.

To turn now to the practical implications of this paper. Hitherto stress seems to have been laid in the literature and in practice upon the desirability of using in the induction process steel having a sorbitic structure. For certain purposes it may be necessary to start out with such a structure. There is reason to suppose, however, that steels having a spheroidized or a coarse pearlitic structure, if heated rapidly and quenched immediately, so that pseudomorphs of the structures are retained, may be ideal for induction hardening. In short, the usefulness of the new process might be considerably widened if less stress were placed on the need for diffusion to occur before quenching. What we have to learn as a result of experience is where best to apply the "new" structures placed at our disposal by the "new" process.

Much work remains to be done to explain the structures which have been obtained. It is believed, however, that sufficient evidence has been given to support the statement with which this paper opened, namely, "Induction heating provides the engineer with means for raising the temperature of steel so rapidly that the point is almost reached where the steel, after heating, can be quenched before any change has occurred in it, other than that of alpha iron to gamma iron".

ACKNOWLEDGMENT

The writer wishes to express his appreciation of the assistance given him by Messrs. J. S. Edgar and W. McIntyre of Thompson Products Limited, of St. Catharines, Ontario, in providing means for the heat treatment of the samples referred to in this paper, and for the help given him by members of the staff of the Department of Engineering and Metallurgy of the Ontario Research Foundation, particularly Misses P. Mudrick, E. Bissonette and J. Brown, who were instrumental in preparing the micro-samples and taking the photomicrographs which illustrate this paper.

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## DISCUSSION

**Written Discussion:** By Arthur E. Focke, research metallurgist, Diamond Chain and Manufacturing Co., Indianapolis, Ind.

We have studied this paper by Mr. Ellis with great interest. Most of us who are using the induction method of heat treating are so busy applying it to specific jobs that we have not spent as much time as we should have on the fundamentals.

We agree with Mr. Ellis that it would be a mistake to insist that the steel for all parts which are to be induction hardened must have a "predominantly sorbitic or normalized" structure. We consider induction hardening first for those parts which would be difficult if not essentially impossible for us to harden satisfactorily in any other way.

But, in addition, there are a large number of jobs for which the induction hardening process should be considered because of its economic advantages. Such jobs must be figured solely on a dollar and cents basis and since the "predominantly sorbitic or normalized" structure does not usually provide the best machining—in fact, such structures may be very difficult to cut in production—the increased machining cost might more than offset the advantage for the induction method of heating. Of course, the parts could be cut from annealed stock and then pretreated to produce the desired sorbitic structure

before induction hardening, but it is clear that with this procedure most of the advantages for the induction method would be lost.

It was only after considerable experimentation that we accepted our first production job for induction hardening on the basis of using 1045 in the hot-rolled condition but our success with this and later jobs has convinced us that for a very large number of our parts the "sorbitic or normalized" initial structure is not essential.

We feel, also, that the unusual properties provided by parts properly induction hardened offer a large field of application for this method. For example, no one in his right mind would make a part of 1045, heat it in the conventional manner, quench it drastically enough to produce a file hard surface with a Rockwell "C" hardness over 60 and attempt to use it in severe service without tempering. Yet this can be done with induction hardening and thousands of parts so treated are performing satisfactorily in the severe requirements of combat equipment.

As a measure of the unusual properties of these induction heated parts, we have set them up in a heavy vise, hit them repeatedly on the hardened edge with a sledge hammer and caused them to take definite permanent set without any evidence of chipping or breaking. We do not know how much of this unusual combination of hardness and toughness is caused by the unusual form of the martensite and how much may be caused by non-uniform carbon solution. Also, we do not know exactly how the wear resistance of such induction heated parts compares with that of conventionally hardened parts of the same or higher surface carbon.

We feel that a very important fundamental research program could be set up on the basis of induction hardening a simple section which could be tested in a manner which would give quantitatively comparable data on the static strength and toughness, impact resistance, fatigue endurance limit and wear resistance between various steels, and between the same steel with various initial structures treated to produce the same or various final structures.

It is for these reasons that we appreciate this contribution by Mr. Ellis and we hope that he may find it possible to continue fundamental research in this field.

**Written Discussion:** By G. Letendre, director, Department of Mining and Metallurgy, Laval University, Quebec, Canada.

Mr. Ellis' paper entitled "Pseudomorphs of Pearlite in Quenched Steel" is very interesting indeed and it is to be hoped that the author will be able to do further work on pseudomorphic structures.

A pseudomorphic pearlite in quenched steel would likely be desirable for some types of service since it would be characterized by a combination of greater strength and greater ductility. Moreover, it might serve effectively to cushion the high stresses often developed in the transition zone between the hard martensitic structure and the softer pearlitic structure remaining unchanged after induction heating followed by quenching. However, it seems doubtful whether a pseudomorphic structure would be the ideal structure for a steel which has to resist high velocity impact such as in a projectile.

It was recently noticed during the examination of a chromium-nickel-molybdenum steel containing ferrite areas and tempered martensite that the

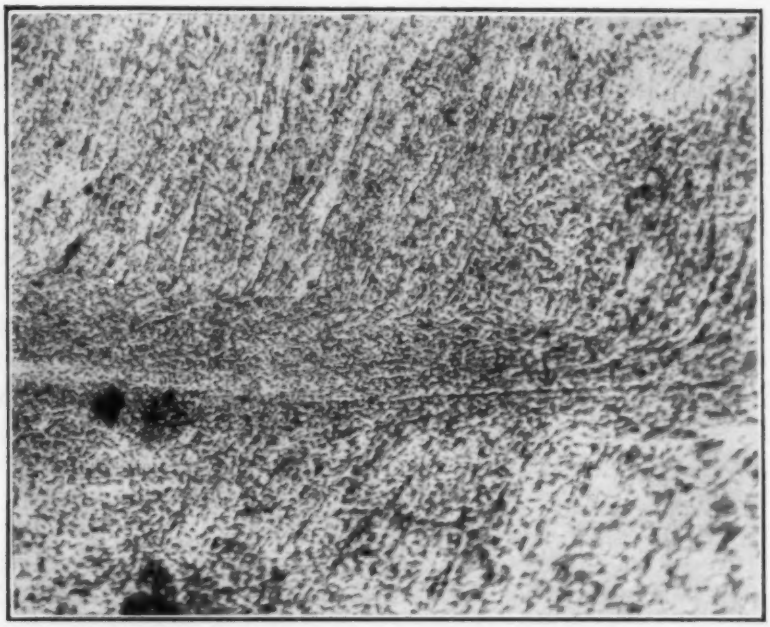

Fig. A—Section from a Nickel-Chromium-Molybdenum Steel Plate Deformed at High Velocity Showing Strain Bands in Two Directions. (Electrolytically Polished, Nital Etched.) × 750.

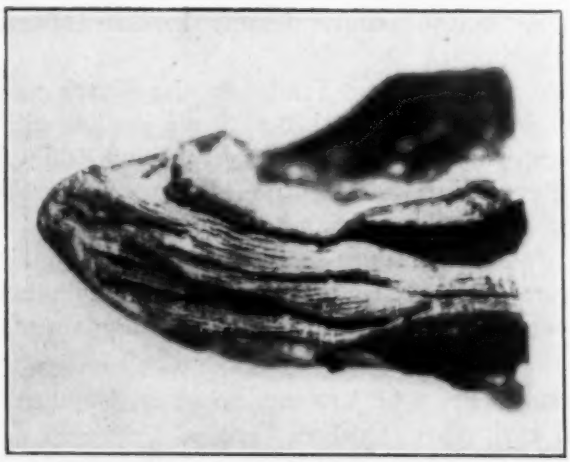

Fig. B—Showing Cleavage Fracture. × 1.5.

metal when deformed at high velocity showed a marked tendency to develop bands of ferrite alternating with bands of tempered martensite (see Fig. A). Such bands when subjected to normal high velocity impact forces are liable to be strongly curved at some points and to develop a secondary slip process as a result of which the more highly deformed slip planes are sometimes damaged and show up as incipient cracks (see arrow, Fig. A). There will result a separation along the weakest slip planes (vertical strain bands) giving rise to a cleavage type of fracture (see Fig. B).

**Written Discussion:** By Roger J. A. Potvin, assistant professor, Department of Mining and Metallurgy, Laval University, Quebec, Canada.

Mr. O. W. Ellis is to be complimented for his excellent work on the "Pseudomorphs of Pearlite in Quenched Steel." The subject is both of practical and theoretical importance since it may pave the way to quick methods of estimating diffusion rates and heats of solution.

It seems of particular interest to compare the results obtained by Mr. Ellis with some of the values calculated from published data on the diffusion rate of carbon in austenite. Derivation from Fick's law shows that the time "t" required for the carbon concentration in a given small area (as measured by the width of the high carbon zones or lamellae) to decrease to half its original value will bear the following relation:

$$t = \frac{3 X_o^2}{4 D}$$

where $X_0$ is the half width of the carbon zones or lamellae and D is the diffusion rate which may be expressed by the equation:

$$D = Ae^{-Q/RT} \qquad (1)$$

where A and Q are assumed to be temperature independent.

In Table A values were calculated taking the most probable estimates for A and Q and assuming that D is independent of carbon concentration since the error thus introduced is small. In column a, A and B were taken as $1.2\times10^{-1}$ cm² per second and 32,000 calories per gram atom respectively.[1] In column b, A and B were given the values of $4.9\times10^{-1}$ cm² per second and 36,000 calories per gram atom[2]. The width of the carbon zones or lamellae was measured directly on Fig. 4 and was found to be approximately $9\times10^{-5}$ cm. The time of "half diffusion", i.e., the time required for the lamellae to double its original width is given under $t_a$ and $t_b$ for the corresponding diffusion rates a and b.

**Table A**

| Temperature of Diffusion Degrees Cent. | D x $10^8$cm² Per Second | | Time in Second X$10^3$ for $X_o = 4.5 \times 10^{-5}$ cm | |
|---|---|---|---|---|
| | a | b | $t_a$ | $t_b$ |
| 900 | 13 | 8.4 | 12 | 18 |
| 850 | 7 | 4.2 | 20 | 36 |
| 800 | 3.8 | 1.3 | 40 | 120 |
| 750 | 1.8 | .8 | 82 | 180 |
| 725 | 1.2 | .5 | 130 | 290 |

Turning back to Fig. 5, it may be noticed that the lamellae in the induction treated sample are roughly twice as wide as those observed in Fig. 4. Referring to the calculated values of the time of "half diffusion" given in the above table, one may conclude at first sight that the time the portion of the sample shown in Fig. 5 has been held at temperature (750 to 850 degrees Cent.) is but a small fraction of a second. Surprisingly enough however, it is stated by the author that the pseudomorphic structure was found in sections taken near the surface of the steel after holding it some 30 seconds at 850 degrees Cent. (1560 degrees Fahr.) before quenching. This difference between the calculated time and the

[1]C. Wells and R. F. Mehl, *Transactions*, American Institute of Mining and Metallurgical Engineers, Vol. 140, 1940, p. 299.

[2]R. M. Barrer, "Diffusion in and Through Solids," The Macmillan Co., 1941.

actual time observed for the diffusion of the carbon is too large to be explained by the gradient of temperature between the induction heated surface and the particular portion which was examined. This lag in diffusion, somewhat analogous to superfusion phenomena but in opposite direction, might be accounted for by introducing a steric factor in equation (1) as follows:

$$D = sAe^{-Q/RT}$$

The steric factor "s" would be dependent upon the surface to volume ratio of the carbide present. In the case of the spheroid structure, "s" would evidently be much smaller than for the lamellar structure which offers a much greater surface for the same volume. As the diffusion progresses, this steric factor seemingly would tend towards unity, and that very rapidly, with the increasing surface of the carbide particles. It might be of interest to study the influence of alloy addition, especially chromium, on such a factor.

**Written Discussion:** By H. B. Osborn, Jr., research and development engineer, Tocco Division, The Ohio Crankshaft Co., Cleveland.

The data and conclusions presented in this paper by Mr. Ellis have been read with extreme interest by the writer and we agree that much work remains to be done to explain the microstructures obtained with short cycle induction hardening. While we have always stressed the advisability of obtaining complete carbide solution and diffusion of carbon we have checked service records on many parts which had not attained such a condition and find no evidence of inferior operations.

Structures have been found in many induction hardened parts which exhibit pearlitic patterns at high magnification. The confusing point, however, is that they are not always ghost images of the original pearlite.

With short heating cycles a satisfactory structure can be obtained even though our present conceptions of just what constitutes a proper structure may be at considerable variance with such results. Pseudomorphs of the original pearlite might well be expected, particularly when the prior structure is coarsely pearlitic. Carbide solution may take place evenly from the adjacent surfaces of two carbide lamellae and progress only far enough so that a microscopic examination of this structure would not show complete loss of the lamellae identity. A portion of the ferrite would thus be converted to austenite which on quenching yields the desired martensite.

The intervening region may be low in carbon due to inadequate saturation but being surrounded by martensite and carbide lamellae, any hardness penetrator would indicate a value which might be an average of a high hardness and the lower hardness characteristics of the structures present. Similar condition would exist on material which had a spheroidized structure prior to induction hardening and we have considerable data to show that complete diffusion of the spheroids is not necessary provided they are reasonably well dispersed and enough carbon has gone into solution to give the desired hardness This is particularly true of higher carbon steels than referred to by Mr. Ellis, especially such analysis as S.A.E. 52100. In fact, the undissolved carbides in such material provide for better wear resistances when used for bearing surfaces.

Induction heating has truly provided us with a means for heating metallurgical parts very rapidly and the metallurgical transformations which occur must be given considerable study. Unfortunately, the time cycle is so short

that we are at an extreme disadvantage in attempting to analyze transformation changes which take place during these cycles.

In previous publications the writer has presented some data on this subject but should like to state herewith a few additional facts which will bear further investigation when the pressure of the war has been removed.

1. Samples of S.A.E. 1045 steel have been treated to temperatures between the lower and upper critical and hardened to expected Rockwell "C" values for such analysis. A microscopic examination of the resulting structure shows a thoroughly diffused martensite and no free ferrite, even though the temperature of the material had never been above the free ferrite equilibrium range prior to quenching.

2. Samples of various analysis have been treated to temperatures well below a lower critical and quenched. Although the equilibrium diagram would not condone a hardening of steel at such temperatures, the material treated as described has definite evidence of hardness and microscopic transformations which theoretically should not take place until critical temperatures have been reached.

3. Recombinations of carbon or graphitization of cast iron to form structures which can be subsequently machined and hardened can be made to take place in a matter of seconds when heated by high frequency current. Conventional methods of treatment require several hours for similar results.

Induction heating has opened up new thoughts in our minds and the facts presented indicate quite clearly that induction heating is somewhat unusual in so far as the metallurgical results are concerned. Most of this is perhaps of academic interest only but it is believed that the higher hardnesses, rapid carbide solution rates, and the finer, more nodular type of martensite inherently characteristic of induction process may be explained as follows:

The major constituents of steel are iron carbide and ferrite. Iron carbide has a higher specific resistance than ferrite and therefore, with a flow of current induced by high frequency, the iron carbide should attain a slightly higher temperature than the adjacent ferrite. Just what this temperature differential might be, we will probably never know, but the mere fact that it does exist creates a driving potential since we have placed the iron carbide on a higher energy level than the ferrite. Obviously anything which will take place under isothermal conditions, upon which the equilibrium diagram is predicated, will most certainly take place faster and more thoroughly under the conditions described above.

## Oral Discussion

T. E. NORMAN:[3] I just want to congratulate Mr. Ellis for drawing our attention to what I believe is something of considerable significance. Also I would like to ask Mr. Ellis if he has any data on volume changes resulting from transformation of austenite to martensite of this pseudomorphic variety. That is, is the volume change as great as it is when austenite changes to martensite of the usual type? It seems to me that this would have considerable relation to the degree of residual stress which we end up with in the quenched martensite.

[3]Metallurgist, Climax Molybdenum Co., Denver, Colo.

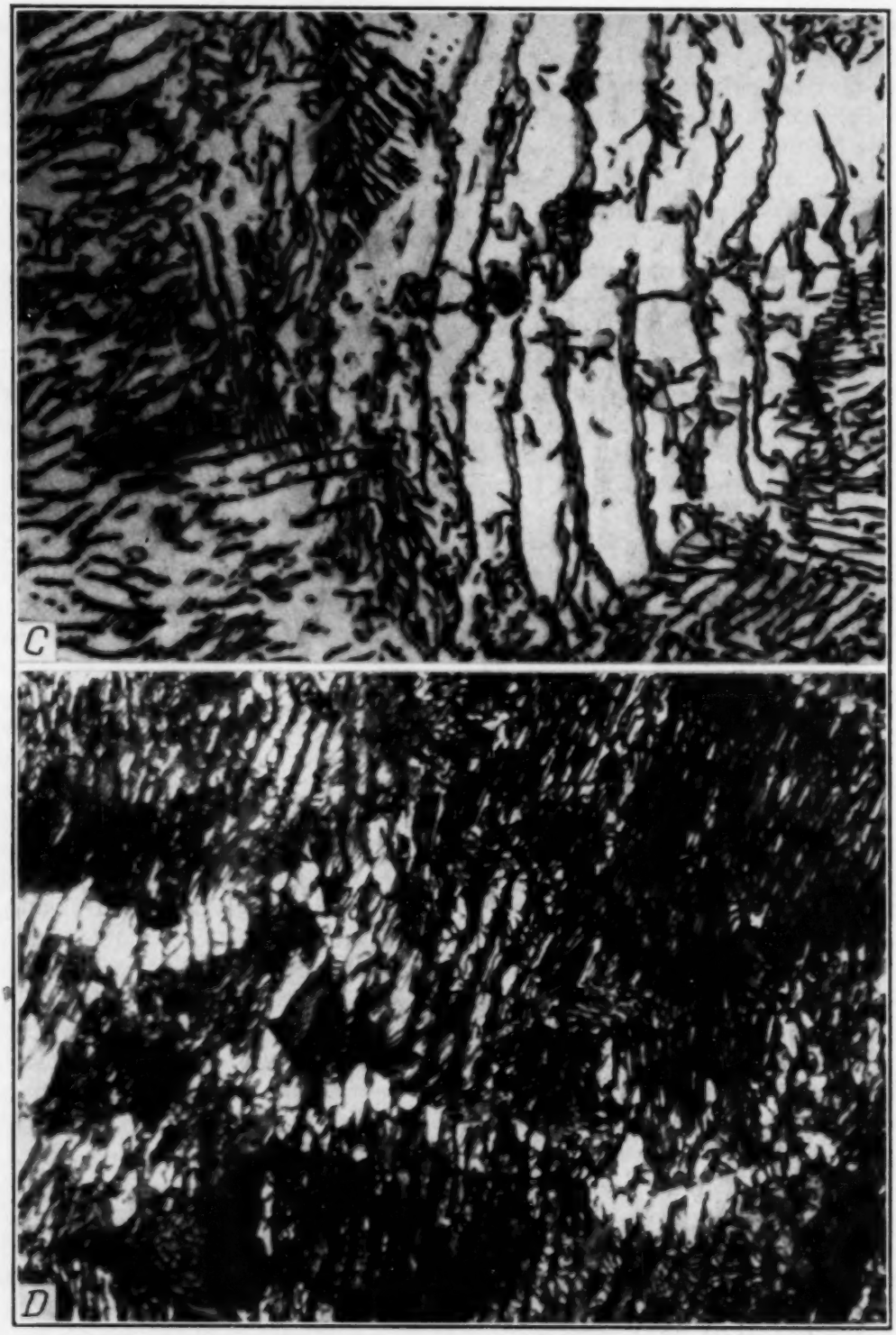


Fig. C—Fine Pearlite Lamellae Across a Coarser Pearlite Produced by Having the Sample Above the Critical Temperature for a Very Short Time. Picral Etch. × 2000.

Fig. D—Fine Pearlite and Ferrite Grains Developed Across Remaining Coarser Pearlite Lamellae Produced by Rapid (Induction) Heating and a Hot Quench. Picral Etch. × 2000.

Also, is there any difference in the temperature at which this martensite begins to transform? In the meetings here, particularly on Monday, we learned quite a bit about the temperature at which martensite begins to transform. Possibly with austenite in the condition that Mr. Ellis had it when he quenched it, there would be a difference in the temperature of martensite transformation, together with a corresponding difference in the amount of residual stress which results in the quenched martensite.

CHARLES WALTON:[4] Some time ago I observed a structure which is in line with this interesting paper. This occurred in an induction heat treated cast iron. The structure was a medium pearlite to begin with and was rapidly heated to above the critical and rapidly cooled to 1000 or 1100 degrees Fahr. (540 or 595 degrees Cent.). In the resulting structure, the original medium pearlite lamellae were interlaced by a very fine pearlite which was only resolved with an oil immersion lens. The original lamellae were somewhat knobby, indicating a partial resolution. The very fine pearlite tended to be continuous right across the original carbides.

The two photomicrographs show the beginning stage and a well developed stage of this phenomena. Fig. C contains only small scattered patches and some individual plates of the fine pearlite while Fig. D, an area heated to a higher temperature than that in Fig. C, contains a well developed matrix of pearlite and ferrite superimposed over the original pearlite. The ferrite tends to outline areas which had no indication in the original pearlite.

### Author's Reply

Replying first to Mr. Walton's comment on the paper and his reference to pearlite in quenched induction-heated cast iron, in view of the fact that I had been able to obtain pearlite at will in quenched induction-heated steel, I had shaped up for me what was in essence an armor piercing shot of rather poor quality cast iron, nevertheless an iron having a pronounced pearlitic structure with the usual graphite and other nonmetallic inclusions present in the matrix. This "shot", on quenching after rapid induction heating, retained the pearlite as a pseudomorph. I did not examine the structure of this "shot" with the care with which Mr. Walton evidently examined his sample, as is evidenced by Figs. C and D which accompany his written contribution. In this connection, however, I would like to refer to Figs. 4 and 5 in my paper again, because a comparison of those two figures brings out the point made by Mr. Walton, viz., that in material before treatment the carbide lamellae are very clearly defined, while in material after rapid induction heating and quenching the carbide lamellae lack their original definition. The structure in steel, as in cast iron, after quenching, while definitely pearlitic, has lost some of its clearness due to the "knobbiness" to which Mr. Walton referred.

Dealing with Mr. Norman's points regarding volume changes and internal stresses, we have had no opportunity to work on volume changes or internal stresses. However, there is some evidence to support the view that hardened steel having a pseudo-pearlitic structure, resulting from rapid induction heat treatment, is freer from internal stresses than steel having a martensitic struc-

[4]Metallurgist, Association of Manufacturers of Chilled Car Wheels, Chicago.

ture, also resulting from rapid induction heat treatment. It was partly because of this observation that we felt it desirable to present this paper.

With regard to temperatures of transformation, the conditions under which this work was carried out were such as to make work along these lines impossible. I am hoping that one day someone, if not I, will be able to pursue these very interesting and important matters.

Consideration of Mr. Focke's interesting contribution follows very naturally

Fig. E—Photomicrograph of Drastically Cold-Worked Steel.

the remarks made in the last two paragraphs, because we feel that his success in the application of S.A.E. 1045 steel in the hot-rolled condition is intimately related to the probable retention of a pseudomorph of the original hot-rolled structure of the steel in the finished parts. This pseudomorph, though having a Rockwell "C" hardness number in excess of 60, is, in all probability, subject to less internal stress than would be similar parts hardened in the same manner and to the same degree of hardness and consisting of acicular martensite. There is undoubtedly much to be said for the retention as a pseudomorph of such structures as we have discussed immediately above and, independently, in the paper. Although mechanical tests made on drawn induction-hardened steel of the composition referred to in the paper do not indicate any marked differences from those made on samples of the same steel treated by orthodox means, nevertheless shock tests (firing shot at armor plate) all seem to support the view that untempered induction-hardened steels having pseudomorphic structures are much tougher than both induction-hardened steel and steels hardened by orthodox means having martensitic structures. Quantitative information, however, is undoubtedly needed to prove this point conclusively.

The above observations on shock tests should dispel, in some measure,

Dr. Letendre's doubt regarding the applicability of pseudomorphic structures to projectiles.

We have found it somewhat difficult to interpret Dr. Letendre's remarks to the effect that a pseudomorphic pearlite "might serve effectively to cushion the high stresses often developed in the transition zone between a hard martensitic structure and a softer pearlitic structure remaining unchanged after induction heating followed by quenching." We have obtained no evidence to suggest that the pseudomorph of pearlite resulting from rapid heating and immediate quenching is other than what may be described as a heterogeneous martensite having the appearance of pearlite. This pseudomorph is by no means soft; Rockwell "C" hardness values of 65 are not unusual in steels having a pseudomorphic structure. We have gained the impression, however, that the untempered pseudomorph is tougher (more resistant to shock) than more homogeneous martensite, such, for example, as that obtained as a result of orthodox methods of heat treatment.

Dr. Letendre's photomicrograph of the structure of an alloy steel which had been deformed at high velocity is quite interesting, because it is redolent of pearlite. It would have been useful to have seen, for comparison, the structure of this steel before it had been plastically deformed, because one gains the impression on examining Dr. Letendre's photomicrograph that the structure therein is just what one might have expected, for example, to obtain as a result of the drastic cold working of steel having the appearance shown in Fig. E.

To Dr. Potvin we must apologize for not having made it clear that, after it had reached maximum temperature, the shot was *cooling* during the 30 seconds which elapsed before it was quenched. It was not held *at* 850 degrees Cent. (1560 degrees Fahr.) for 30 seconds before quenching. Cooling occurs immediately the supply of power to the coil is interrupted. On this account some modification of Dr. Potvin's calculations will be necessary.

Dr. Osborn's remarks, based as they are on almost as wide an experience in this field as anyone's at the present time, bring out points which serve to emphasize still more clearly the author's contention "What we have to learn as a result of experience is where best to apply the 'new' structures placed at our disposal by the 'new' process." Just the three facts tabulated in Dr. Osborn's contribution to this discussion should be enough to whet the appetite of anyone inclined to the view that we know all there is to know about steel.

# STRUCTURAL CHANGES DURING THE TEMPERING OF HIGH CARBON STEEL

By Dara P. Antia, Stewart G. Fletcher and Morris Cohen

*Abstract*

*Despite the fact that the tempering of plain carbon steel is ordinarily regarded as a comparatively simple process, the prevailing theories of tempering are not consistent with the available data. In order to clarify the many issues, the present research attacks the problem with combined X-ray, metallographic, hardness, magnetic, dilatometric and specific volume studies.*

*The results demonstrate that hardened steel, containing tetragonal martensite and retained austenite, passes through three structural changes on tempering. Tetragonal martensite decomposes during the first stage into an aggregate of ferrite and a transition precipitate. The second stage consists of austenite transformation into an acicular structure with the same state of aggregation as the tempered martensite. During the third stage, the transition precipitate formed during the first two stages decomposes into cementite particles which gradually coalesce until the well-known spheroidized structure is achieved. Stress relief accompanies the three stages of tempering. All of these reactions are time dependent, and occur either isothermally or on heating to the tempering temperature.*

## Introduction

DURING the past few years, the authors have investigated the tempering characteristics of some twenty steels and high-purity iron-carbon alloys, representing a systematic series of plain carbon, nickel and nickel-molybdenum types. The compositions of these materials ranged from 0.5 to 1.5 per cent carbon, and 0 to 5 per cent nickel with 0 to 0.5 per cent molybdenum. The structural changes during tempering were found to be basically the same in all these materials, although there were some variations in details, as would

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be expected. Before considering the specific effects of chemistry on these structural changes, however, it appears advisable to focus attention first on the fundamental nature of the changes themselves. This, then, is the principal object of the present paper. Although, in order to simplify the discussion, only two steels and one high-purity alloy are selected to form the basis of reasoning, it must be emphasized that the picture thus revealed is entirely consistent with the tempering behavior of the other compositions studied.

The three materials chosen are high in carbon so that the tempering effects may be shown to best advantage. One steel is a commercial plain carbon grade, containing 0.94 per cent carbon, while the second is a 1.0 per cent carbon, 4.8 per cent nickel steel. In the hardened state, these two steels contain widely different ratios of retained austenite to martensite without exhibiting too much difference in structural stability; and hence, comparisons of their tempering behavior greatly facilitate the disentanglement of overlapping changes brought about by retained austenite and martensite decomposition. The high-purity iron-carbon alloy, containing 0.95 per cent carbon, is included because it permits comparison with the straight carbon steel.

## Theories of Tempering

The literature on the tempering of high carbon steel is so voluminous that no attempts will be made to review it here. An excellent survey of the subject has been published by Epstein (1)*, and the reader is referred to this source for the necessary background to the existing ideas on the mechanism of tempering.

The evidence is quite clear that, starting with a hardened structure composed essentially of tetragonal martensite and retained austenite, high carbon steels undergo three important stages during tempering. (Excess ferrite or cementite and nonmetallic inclusions may be disregarded for the purpose of this discussion.) These stages have been disclosed by measurements of specific volume (2)-(6), dilation (2), (7), (8), (11), magnetization (8)-(14), and electrical resistivity (5), (8). There is also a marked evolution of heat in each of the three stages (11), (15-17). A summary of these data indicate that the three stages occur in the following temperature ranges:

*The figures appearing in parentheses pertain to the bibliography appended to this paper.

First stage, 200—350 degrees Fahr. (95—175 degrees Cent.)
Second stage, 450—550 degrees Fahr. (230—290 degrees Cent.)
Third stage, 550—750 degrees Fahr. (290—400 degrees Cent.)

These ranges, of course, are only approximate, since they depend upon the rate of heating and time of tempering as well as upon the type and sensitivity of the measurements. On the other hand, variations in composition and austenization appear to cause little displacement of the temperature ranges, even though the relative intensities of the individual stages may be greatly affected.

There is fairly general agreement that the second stage of tempering is attributable to the transformation of retained austenite. The simultaneous increase in magnetization and volume along with the retarded softening and evolution of heat in this range may be taken as good evidence of retained austenite decomposition. However, the nature of the decomposition product is still obscure; for lack of contrary proof it is usually assumed to be an aggregate of ferrite and cementite (15), (18). It has also been proposed that austenite transforms momentarily into martensite prior to forming such an aggregate (1).

The exact significance of the first and third tempering stages is a matter of dispute, even though it is commonly felt that they are associated with the decomposition of tetragonal martensite into an ultimate aggregate of ferrite and cementite. Honda and Nishiyama (19) propose that the first stage involves the transformation of the tetragonal structure (alpha martensite) into a cubic structure (beta martensite) without the precipitation of the dissolved carbon. This change is pictured as a simple shift of the carbon atoms from the (½, ½, 0) positions which they occupy in the tetragonal lattice* to the (½, ¼, 0) positions which are more spacious. Such a shift would tend to explain the decrease in volume, the merging of the tetragonal diffraction doublets into single cubic lines, the evolution of heat, and would also be expected to have but a slight effect on magnetization—all of which phenomena are so observed during the first stage of tempering. The carbon atoms are then assumed to remain dissolved in the cubic solution until the third stage of tempering when they precipitate to form cementite particles in a ferrite matrix. This postulated structural change is consistent with the observed evolution of heat as well as the simultaneous contraction and decrease in magnetization that identify the third stage.

*This location of the carbon atom in tetragonal martensite has been recently confirmed by Petch (20).

However, there are important objections to the Honda-Nishiyama theory of martensite decomposition. The movement of carbon atoms into larger interstices during the first stage should reduce the degree of lattice distortion and hence cause a measurable softening, but actually a considerable increase in hardness takes place when tetragonal martensite decomposes (15), (21), (22). Moreover, if it is accepted that the cubic martensite thus formed is a single phase (rather than a heterogeneous mixture) there is difficulty in accounting for its intensely dark-etching behavior compared to the light-etching characteristics of tetragonal martensite. Finally, as Hägg (23) points out, the X-ray evidence for the existence of cubic martensite is certainly questionable. Since the degree of tetragonality of quenched martensite, and hence the spacing of the diffraction doublets, is a direct function of the dissolved carbon content, precipitation of carbon from the solid solution during tempering could result in a merging of the doublets into diffuse single lines, which would then be indistinguishable from a cubic pattern. Thus, from the X-ray point of view, a slightly-tetragonal structure having little carbon remaining in solution may easily be mistaken for a cubic structure with all the carbon in solution. Furthermore, the nonappearance of any new lines corresponding to a precipitated phase cannot be accepted as evidence of "carbon still dissolved" in view of the fact that the diffraction method is not particularly sensitive in detecting the presence of a finely dispersed precipitate.

Hanemann and Traeger (7) also postulate a two-step decomposition of martensite, very similar to the Honda-Nishiyama picture, and subject to the same objections. They call the intermediate phase zeta, and conclude that the carbon remains dissolved in this phase until the latter breaks down into ferrite and cementite during the third stage.

On the other hand, Hägg (23) contends that the progressive loss of tetragonality during the first stage is the result of precipitation of carbon from tetragonal martensite, the axial ratio approaching unity as the dissolved carbon approaches zero. He does not speculate on the identity of the precipitated carbon-bearing phase, but others (18), (24)-(26) have assumed it to be cementite. Such precipitation of cementite would be consistent with the hardening and dark-etching characteristics observed during the first stage of tempering, but actual calculations show that cementite formation

would produce a much larger contraction than is actually found when tetragonal martensite decomposes (27). In addition, if cementite precipitates during the first stage, it becomes difficult to explain the third stage. Mere agglomeration of the cementite particles could hardly bring about the marked volume, magnetic and heat effects there encountered. Bain (28) has suggested that a recrystallization of the highly strained ferrite may account for the heat evolution, but the accompanying contraction is much too large to be explained in this way.

Taking a somewhat intermediate stand, Esser and Cornelius (15) suggest that during the first stage tetragonal martensite decomposes into cubic ferrite with the precipitation of cementite molecules. The molecules are then pictured as combining during the third stage to form crystalline cementite. This theory could conceivably account for the observed changes, but suffers from the weakness that there is no independent evidence to substantiate the possible existence of molecular cementite (29). Iron carbide, like other intermetallic compounds, owes its identity to a characteristic crystal structure. While, on the average, there are three iron atoms for each carbon atom in the cementite crystal, the corresponding formula, $Fe_3C$, should not be construed as implying the existence of $Fe_3C$ molecular units. In fact, the known crystal structure of cementite (30) shows no sign of carbon atoms closely attracted to trios of iron atoms. Actually, each carbon atom nestles in the central interstice of a triangular prism, the six corners of which are occupied by iron atoms. These prisms are stacked in such a way that an orthorhombic structure is generated, with each iron atom being shared by two prisms. Hence, on the average, there are three iron atoms per carbon atom, but no $Fe_3C$ molecular units. Since it is equally doubtful that cementite molecules exist when carbon is dissolved in austenite or in tetragonal martensite, the case for molecular precipitation is further weakened.

From the foregoing, it is evident that the structural changes on tempering of plain carbon steel are not as simple as they are implied to be in many textbooks. Not only do major differences of opinion prevail among the principal investigators in this field, but no one of the available theories is completely satisfying. Part of this controversy stems from the fact that several types of measurement must be brought to bear on the problem before a comprehensive picture can be obtained, and this has not been

done by any one investigator. The present research was particularly designed to overcome this difficulty, even though some repetition of scattered previous work was necessary.

## Experimental Details

*Materials Studied* — The compositions of the three materials which constitute the basis of this investigation are given in Table I. The 0.94 per cent carbon steel was purchased in the form of ¾-inch diameter hot-rolled bars. The 0.95 per cent carbon high-purity iron-carbon alloy and the nickel steel were made in laboratory induction furnaces. The former was melted and chill cast in vacuo as a 5.5-pound ingot, while the latter was melted and poured in air as a 30-pound hot-topped ingot.

**Table I**
**Chemical Analyses**

| Designation | Per Cent by Weight | | | | | |
|---|---|---|---|---|---|---|
| | C | Mn | S | P | Si | Ni |
| Commercial carbon steel | 0.94 | 0.33 | 0.015 | 0.009 | 0.13 | nil |
| Iron-carbon alloy | 0.95 | nil | 0.006 | 0.003 | 0.004 | nil |
| Nickel steel | 1.00 | 0.43 | 0.05 | 0.05 | 0.01 | 4.82 |

The commercial carbon steel bars were turned down to 0.240-inch rods prior to heat treatment, while the laboratory ingots were homogenized at 1800 degrees Fahr. (980 degrees Cent.) for 24 hours, then forged into ½-inch rounds. Part of the nickel steel ingot was also forged into ⅞-inch square bars. This forged stock was then annealed and machined down to 0.240-inch round and ½-inch square bars respectively.

*Heat Treatment* — The austenizing temperatures were selected to dissolve all the ferrite and cementite without unduly coarsening

**Table II**
**Hardening Treatments**

| Designation | Section Size Inch | Austenizing Temp. °F. | Austenizing Time Min. | Heating Medium | Quenching Medium | Per Cent Retained Austenite |
|---|---|---|---|---|---|---|
| Commercial carbon steel | 0.240 round | 1500 | 30 | Lead | Water | 13 |
| Iron-carbon alloy | 0.240 round | 1500 | 30 | Lead | Water | 9 |
| Nickel steel | 0.240 round | 1700 | 30 | Carbonaceous muffle | Oil | 37 |
| Nickel steel | ½ square | 1700 | 30 | Carbonaceous muffle | Oil | 48 |

the austenite grains. The hardening conditions are tabulated in Table II. In each instance, the quenching rate was sufficiently rapid to suppress proeutectoid separation and pearlite formation.

The tempering treatments were of the following types:

(a) Continuous tempering survey runs. These consisted of heating to 1000 degrees Fahr. (540 degrees Cent.) at 5 degrees Fahr. (2.8 degrees Cent.) per minute and cooling at the same rate for dilation and magnetic measurements.

(b) Interrupted tempering survey runs. These involved heating to progressively higher temperatures (usually at 50 degrees Fahr. (28 degrees Cent.) intervals) for 5-minute periods with recurrent cooling to room temperature for X-ray diffraction, specific volume, metallographic and hardness studies.

(c) Isothermal tempering runs. Measurements of dilation and magnetization were made at temperature, while periodic cooling to room temperature permitted X-ray diffraction, specific volume, metallographic and hardness measurements.

(d) Special cyclic runs. These were devised to follow the development of cementite on tempering as revealed by its Curie point behavior.

Whenever rapid heating or accurate timing was essential, the tempering was executed in liquid baths; otherwise air furnaces were used. The temperature control and measurements were usually better than $\pm 2$ degrees Fahr. (1 degree Cent.) and invariably better than $\pm 5$ degrees Fahr. (3 degrees Cent.).

*Types of Measurements* — The magnetic and dilation measurements (respectively $\pm 0.2$ per cent and $\pm 10^{-5}$ inches per inch relative accuracy) were conducted simultaneously on cylindrical rods, 4¼ inches long by 0.240 inch in diameter. Applied field strengths for the magnetic measurements ranged from 100 to 1500 gauss, with most of the work being done at 265 and 1000 gauss. A complete description of the apparatus and procedure has been published elsewhere (31).

Two types of X-ray diffraction observations were carried out employing a medium-range focussing camera and chromium radiation. According to a previously published technique (32), exposures were made through a calibrated aluminum filter to permit retained austenite determinations ($\pm 1$ per cent austenite) from the relative intensities of the diffraction lines. Platinum powder was then sprinkled on the surface of the specimens and new ex-

posures made sans the aluminum filter. The platinum provided reference lines for reliable parameter measurements ($\pm$0.002 A.U.).

The metallographic, hardness ($\pm$¼ $R_c$ point), and specific volume ($\pm$0.00002 c.c. per gram) techniques are too well known to be described here. In the case of the nickel steel, these measurements as well as the X-ray diffraction determinations were conducted on ½×½×⅝-inch specimens, while only 0.240-inch diameter specimens were used for the plain carbon materials.

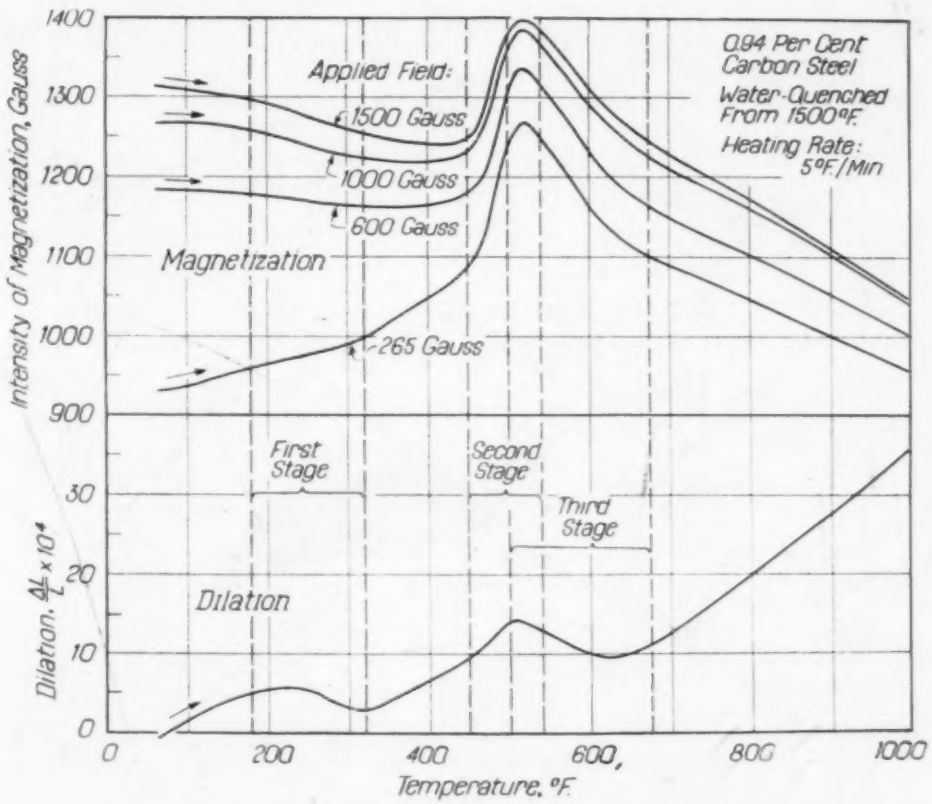


**Fig. 1—Magnetization and Dilation Curves on Continuous Heating of 0.94 Per Cent Carbon Steel After Water Quenching from 1500 Degrees Fahr. (815 Degrees Cent.). Heating Rate: 5 Degrees Fahr. Per Minute. Note the Three Stages of Tempering and the Effect of Field Strength on the Magnetic Curves.**

## Experimental Results

*Continuous Tempering Survey Runs—Measurements at Temperature* — In the hardened condition prior to tempering, all the specimens under consideration are composed completely of tetragonal martensite and retained austenite. The amounts of retained austenite are given in Table II. Curiously enough, the

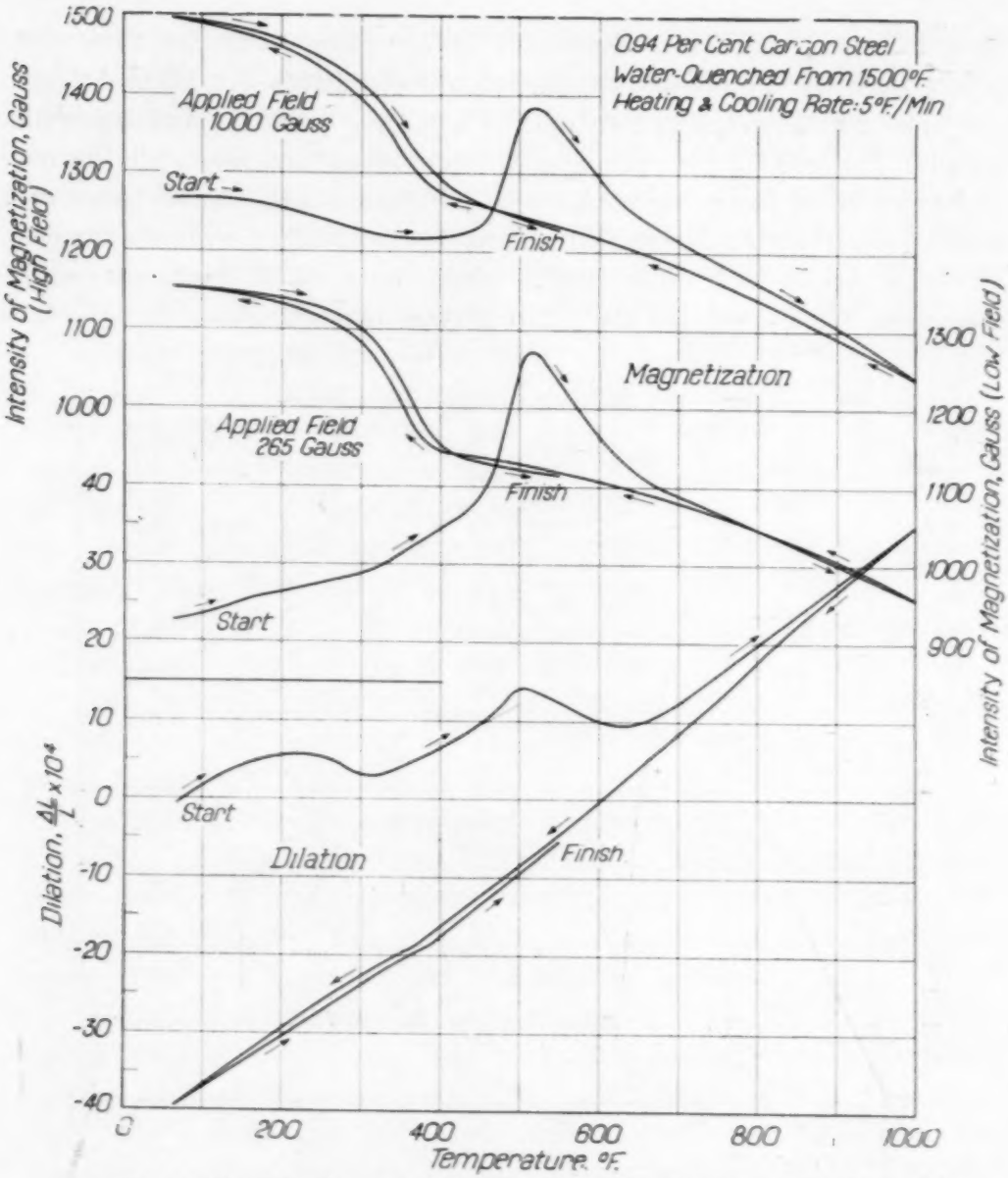


Fig. 2—Magnetization and Dilation Curves on Continuous Heating and Cooling of 0.94 Per Cent Carbon Steel After Water Quenching from 1500 Degrees Fahr. (815 Degrees Cent.). Heating and Cooling Rate: 5 Degrees Fahr. Per Minute. Note the Reversibility of the Cementite Curie Point.

retained austenite content in the nickel steel depends upon the specimen size.

Figs. 1 to 4 illustrate typical continuous survey runs made on the three materials. Only heating curves for the commercial carbon steel are shown in Fig. 1 to demonstrate the effect of applied field strength on the changes in magnetization. It will be observed that there is a marked similarity in the magnetic curves at the three higher fields (600 gauss and above), but the nature of the curve

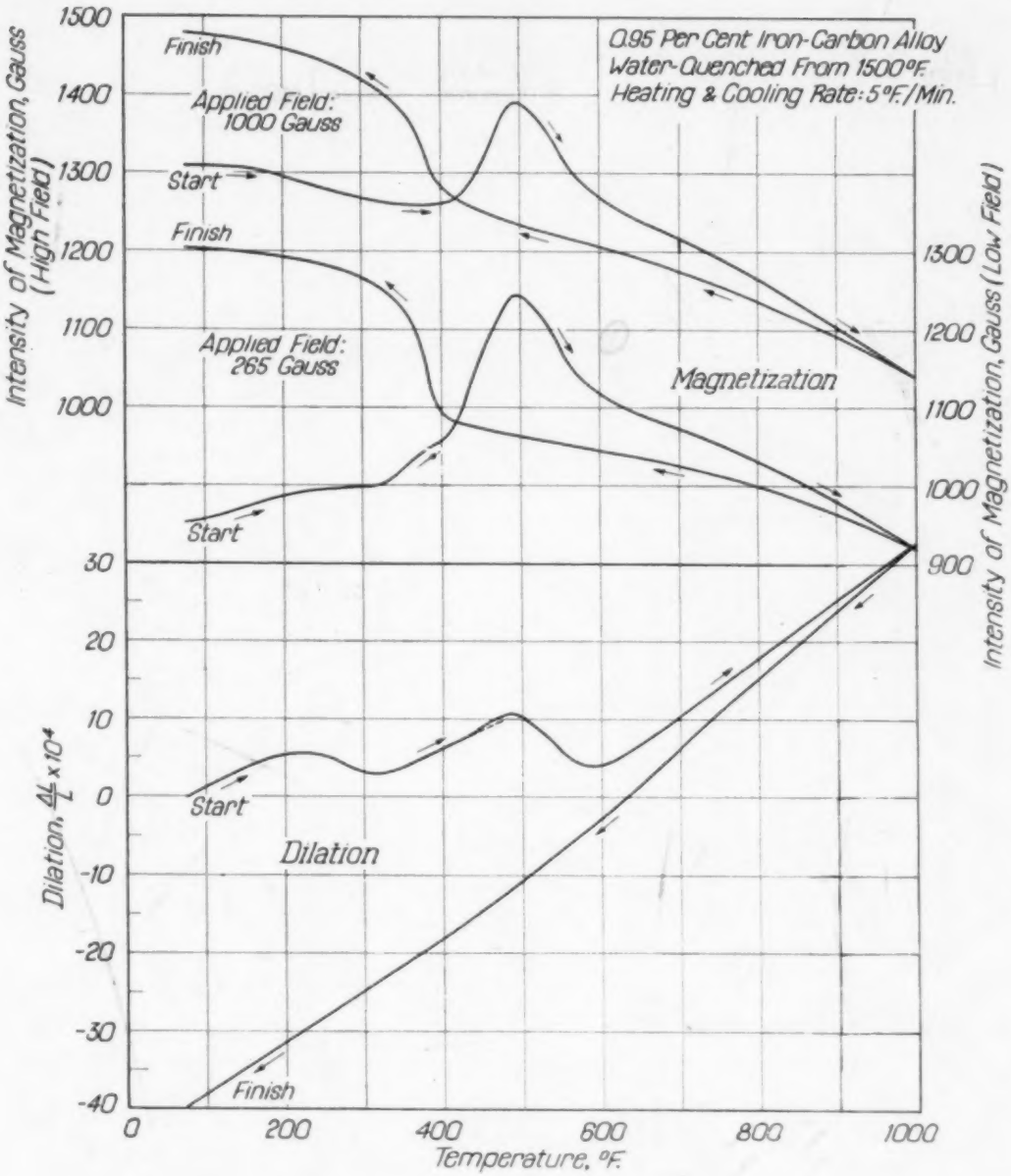


**Fig. 3—Magnetization and Dilation Curves on Continuous Heating and Cooling of 0.95 Per Cent Iron-Carbon Alloy After Water Quenching from 1500 Degrees Fahr. (815 Degrees Cent.). Heating and Cooling Rate: 5 Degrees Fahr. Per Minute.**

at the low field of 265 gauss is quite different. This dissimilarity exists because at low fields such factors as internal stresses and stress relief influence both the intensity of magnetization and its dependence on temperature, while these factors become less and less influential as the field strength is increased to approach magnetic saturation (40). Hence, comparison of high and low field magnetic curves often yields information not obtainable from one

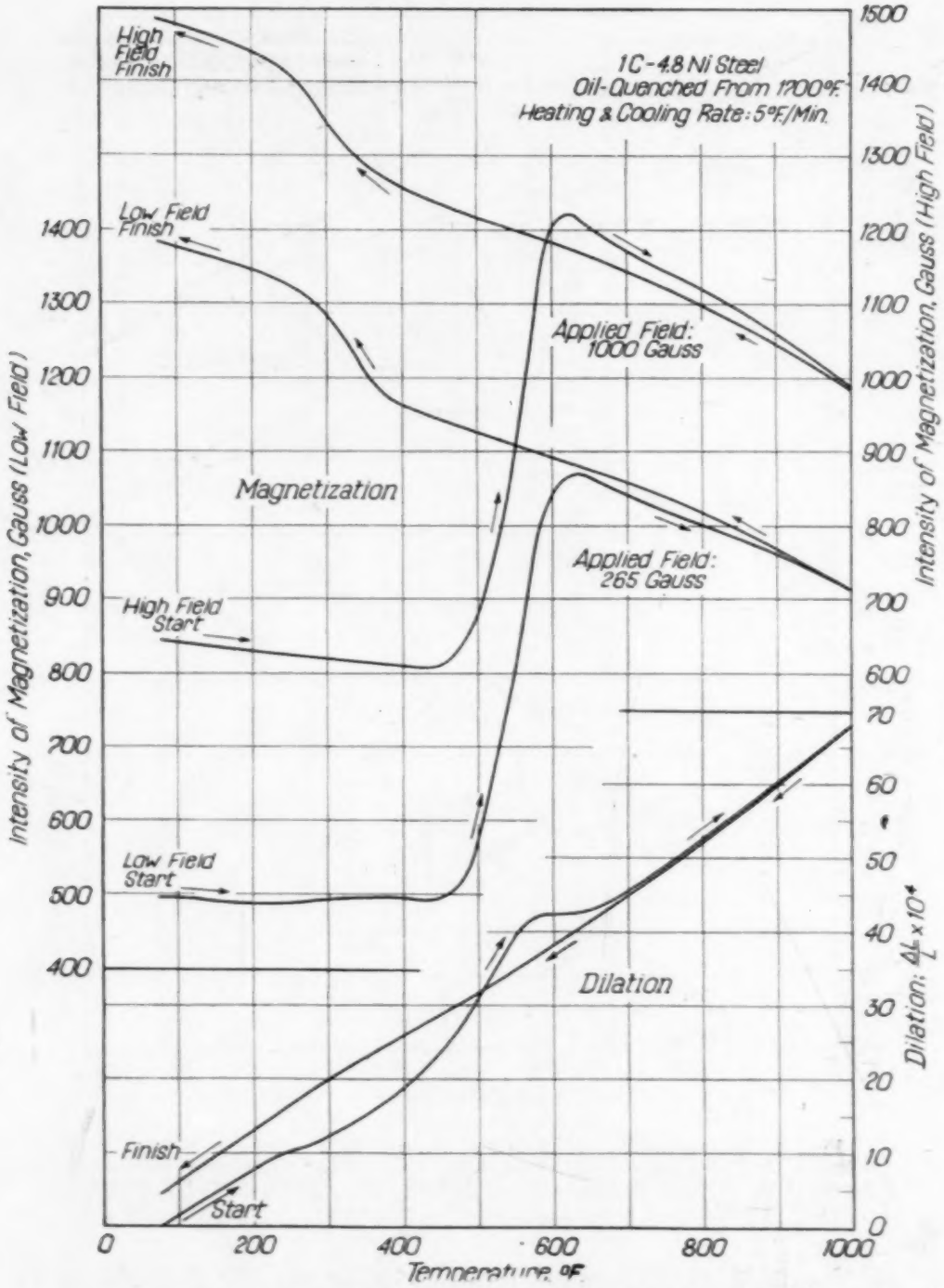


Fig. 4—Magnetization and Dilation Curves on Continuous Heating and Cooling of Nickel Steel After Oil Quenching from 1700 Degrees Fahr. (925 Degrees Cent.). Heating and Cooling Rate: 5 Degrees Fahr. Per Minute.

curve alone. For this purpose, measurements at 1000 and 265 gauss are usually sufficient.

The three tempering stages indicated in Fig. 1 are also evident

in Figs. 2 to 4, where both heating and cooling curves are shown for the three materials. It is immediately seen from Figs. 2 and 3 that the tempering characteristics of the 0.94 per cent carbon steel and the 0.95 per cent carbon high-purity alloy are virtually identical. This correlation, as well as many others not reported here, clearly shows that the common elements in plain carbon steel, other than iron and carbon, have no appreciable effect on the mechanism and rate of tempering.

In these straight carbon materials, the first stage of tempering occurs from about 180 degrees Fahr. (80 degrees Cent.) to 320 degrees Fahr. (160 degrees Cent.), and is characterized by a marked decrease in length and a very slight decrease in magnetization. (It must be remembered that these effects are here recorded *during* heating, and hence are superimposed on the normal temperature-dependent curves.) The second stage takes place between 450 degrees Fahr. (230 degrees Cent.) and 540 degrees Fahr. (280 degrees Cent.), and is represented by a large increase in magnetization and a small expansion. Before the second stage is complete, the third stage of tempering sets in, taking place between the temperatures of 500 degrees Fahr. (260 degrees Cent.) and 675 degrees Fahr. (360 degrees Cent.), and resulting in large decreases in magnetization and in length. Actually, the third stage may continue to a minor degree well above 675 degrees Fahr. (360 degrees Cent.), since the cooling curves between 1000 degrees Fahr. (540 degrees Cent.) and 675 degrees Fahr. (360 degrees Cent.) do not generally coincide with the prior heating curves On further cooling from 1000 degrees Fahr. (540 degrees Cent.), the magnetization and dilation curves are quite normal until reaching a temperature of about 400 degrees Fahr. (205 degrees Cent.). Here there is a conspicuous increase in magnetization, and a slight change in slope of the contraction curve. These effects are caused by the transition of cementite from its paramagnetic to ferromagnetic state ($A_0$ transformation in the iron-carbon diagram). The dilation effect noted here has been fully discussed elsewhere (39). That this inversion is actually a Curie point and not due to retained austenite decomposition (which conceivably could bring about a similar magnetic change) is attested by the relatively minor expansion, and by the reversibility of the reaction on reheating, as demonstrated in Fig. 2.

It should be noted that the normal temperature coefficient of

magnetization is negative. However, as shown in Fig. 1, the coefficient is positive at low applied fields over the temperature range prior to the second stage of tempering. (This is true only on the first heating subsequent to quenching.) At high field strengths, the coefficient over this same temperature range is negative, as it should be. It is believed that the general increase in magnetization when measured at low fields is attributable to the relief of internal stresses, but this will be discussed in more detail later.

The very same type of phenomena are exhibited by the nickel

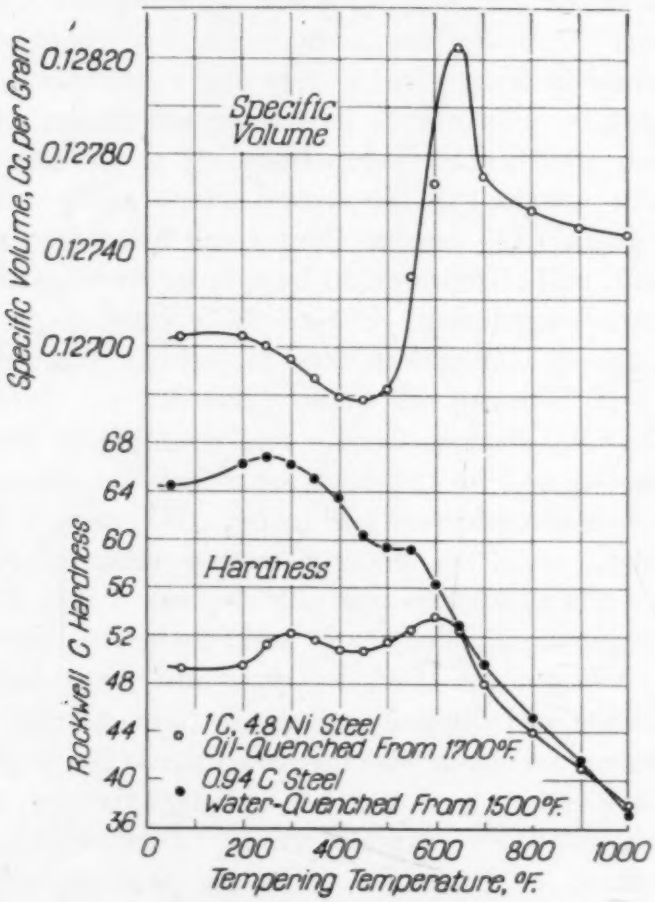


**Fig. 5—Specific Volume and Hardness Curves After Tempering Progressively for 5-Minute Periods at the Indicated Temperatures. Specimens Cooled to Room Temperature Between Temperings for Measurement.**

steel curves in Fig. 4, except that the second stage appears to be more pronounced and the first and third stages less so. The temperature ranges of the first and third stages are hardly affected by the presence of nickel, but the second stage persists to about 650 degrees Fahr. (345 degrees Cent.) instead of 540 degrees Fahr.

(280 degrees Cent.). This persistence tends to obscure much of the third stage reaction. The decreased amount of martensite likewise results in a less pronounced first stage.

The temperature ranges cited above are not to be taken as definite limits. They really constitute the range of maximum

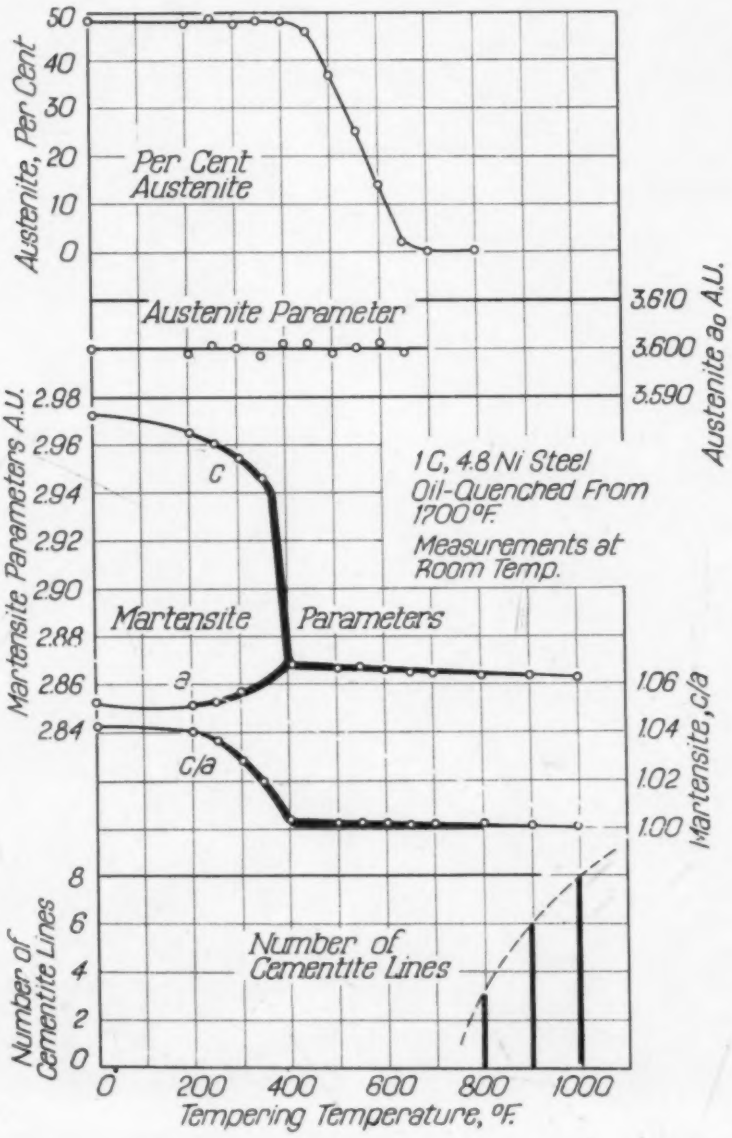


**Fig. 6—X-Ray Diffraction Measurements on the Nickel Steel Specimen Used for Fig. 5.**

change for each stage at the particular heating rate of 5 degrees Fahr. (2.8 degrees Cent.) per minute used in this investigation. Faster heating rates displace the ranges to higher temperatures;

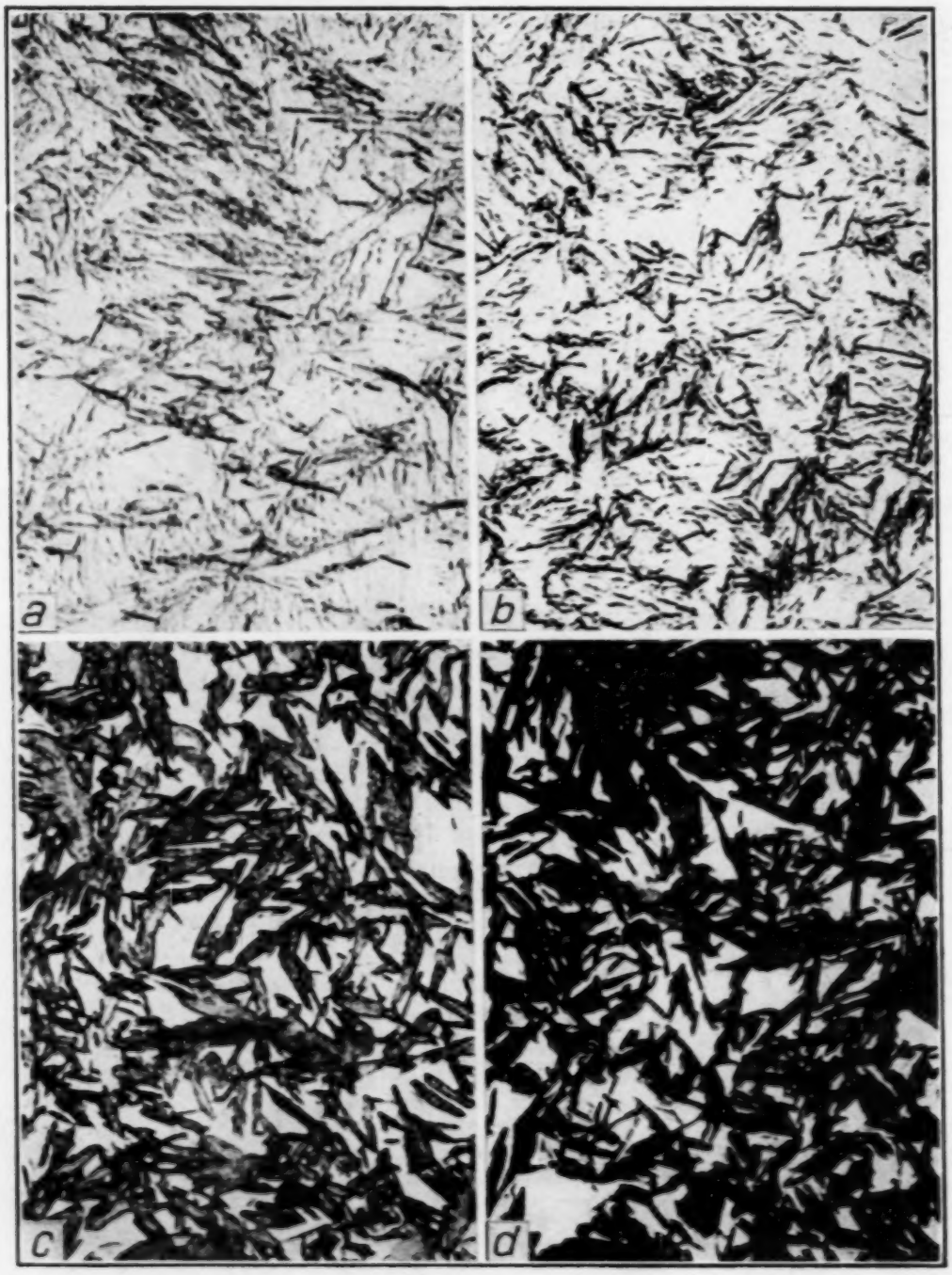


Fig. 7—Microstructures of Nickel Steel, Oil-Quenched from 1700 Degrees Fahr. (925 Degrees Cent.). Etched with Nital. × 1000. (a) As Quenched; (b) Tempered 5 Minutes at 250 Degrees Fahr. (120 Degrees Cent.); (c) Tempered 5 Minutes at 350 Degrees Fahr. (175 Degrees Cent.); (d) Tempered 5 Minutes at 400 Degrees Fahr. (205 Degrees Cent.).

that is, the underlying reactions which cause the three stages of tempering are time dependent.

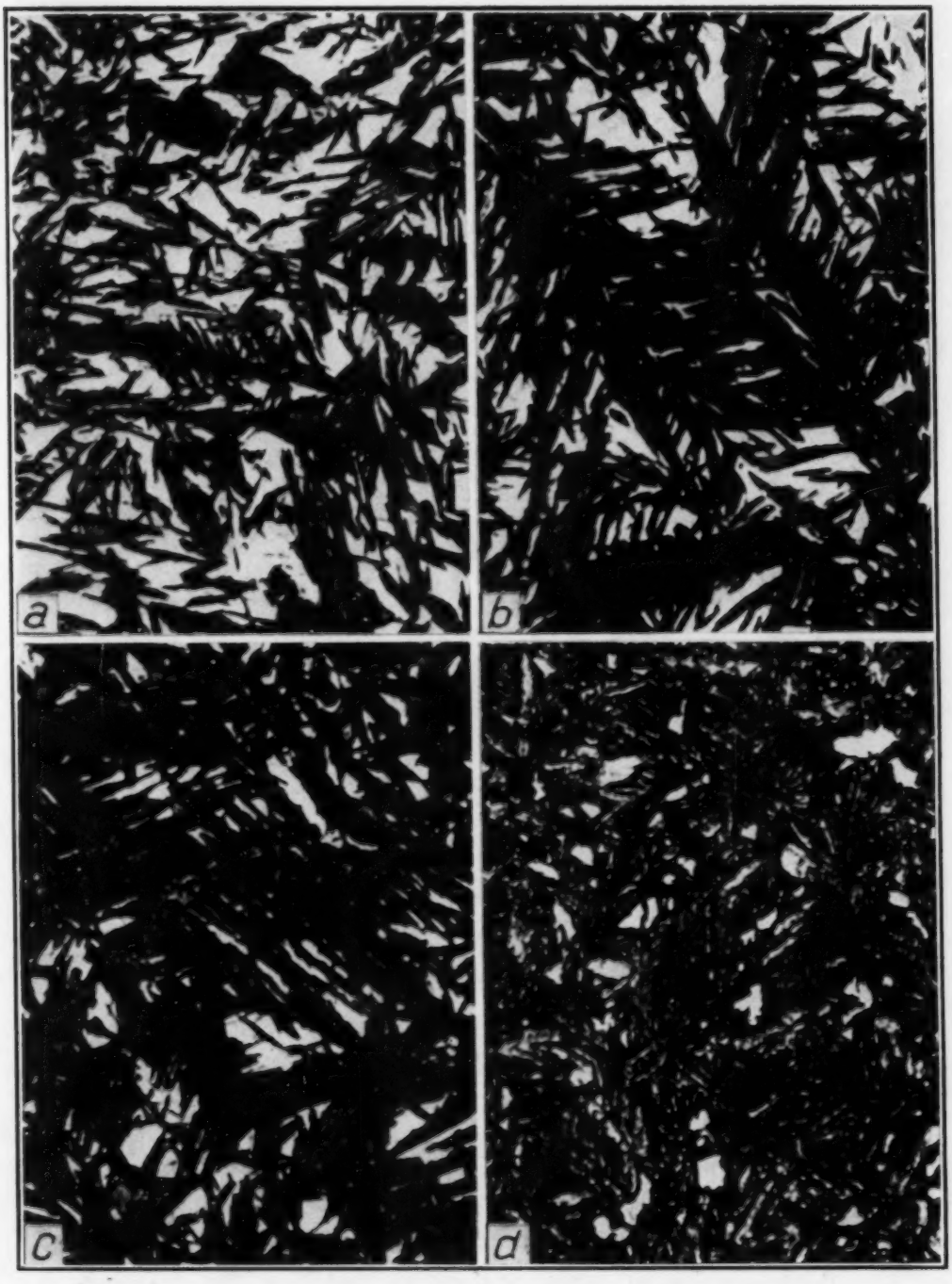


Fig. 8—Microstructure of Nickel Steel, Oil-Quenched from 1700 Degrees Fahr. (925 Degrees Cent.). Etched with Nital. × 1000. (a) Tempered 5 Minutes at 500 Degrees Fahr. (260 Degrees Cent.); (b) Tempered 5 Minutes at 550 Degrees Fahr. (290 Degrees Cent.); (c) Tempered 5 Minutes at 600 Degrees Fahr. (315 Degrees Cent.); (d) Tempered 5 Minutes at 650 Degrees Fahr. (345 Degrees Cent.).

*Interrupted Tempering Survey Runs—Measurements at Room Temperature* — The three stages of tempering may be revealed even more clearly by specific volume measurements at room tem-

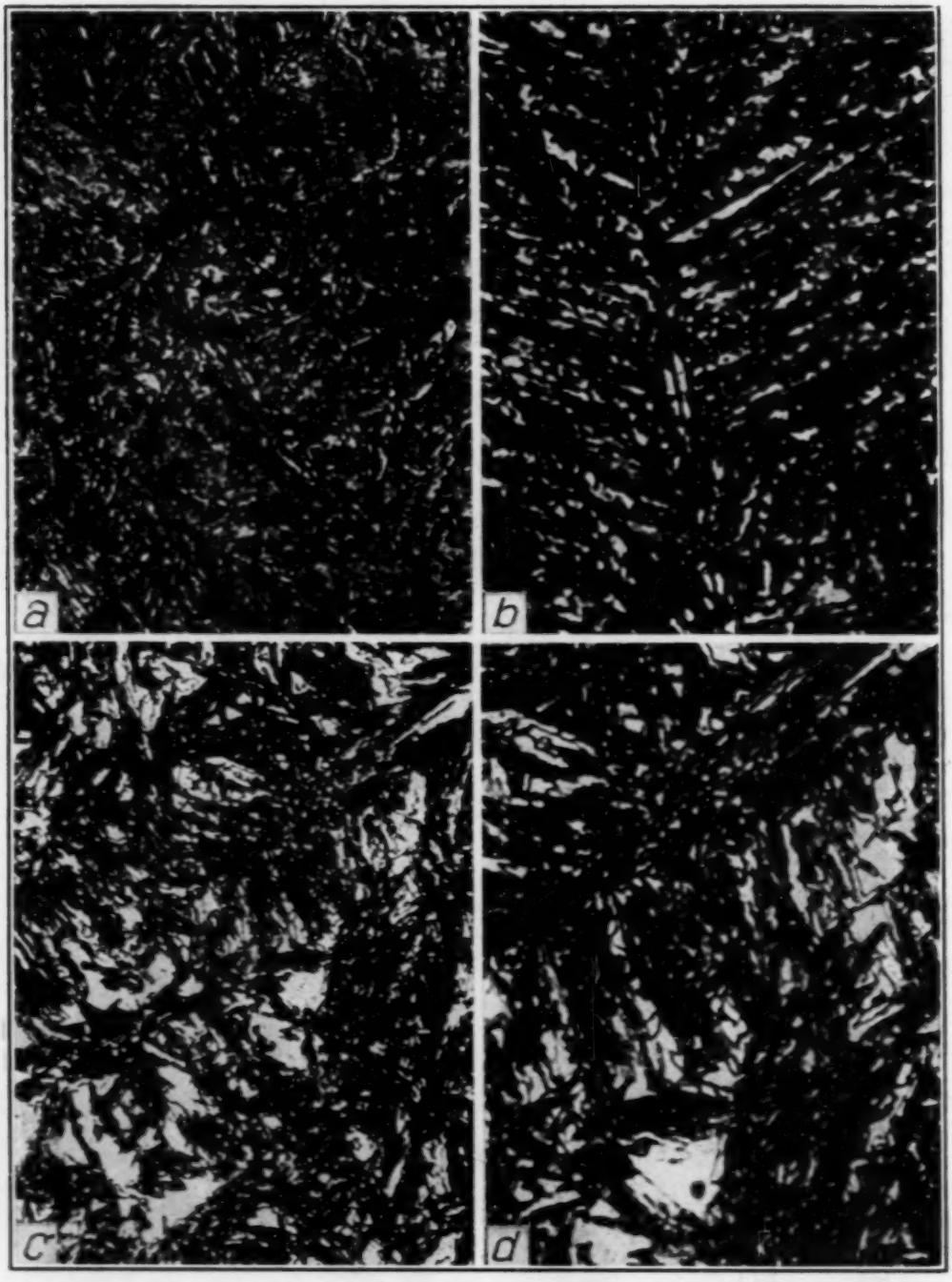


Fig. 9—Microstructure of Nickel Steel, Oil-Quenched from 1700 Degrees Fahr. (925 Degrees Cent.). Etched with Nital. (a) Tempered 5 Minutes at 700 Degrees Fahr. (370 Degrees Cent.), × 1000; (b) Tempered 5 Minutes at 700 Degrees Fahr. (370 Degrees Cent.), × 2000; (c) Tempered 5 Minutes at 1000 Degrees Fahr. (540 Degrees Cent.), × 1000; (d) Tempered 5 Minutes at 1000 Degrees Fahr. (540 Degrees Cent.), × 2000.

perature because temperature coefficient effects are thus eliminated. This is shown for the nickel steel in Fig. 5. In view of the progressive nature of the tempering treatments adopted in this case, the

temperature ranges must not be expected to coincide exactly with those of the continuous heating curves in Fig. 4, but the contraction, expansion, and subsequent contraction are strikingly evident.

The same ½×½×⅝-inch specimens used for these volume measurements were available for hardness, X-ray diffraction and metallographic observations. Fig. 5 also contains the hardness results obtained on these nickel steel specimens, as well as corresponding

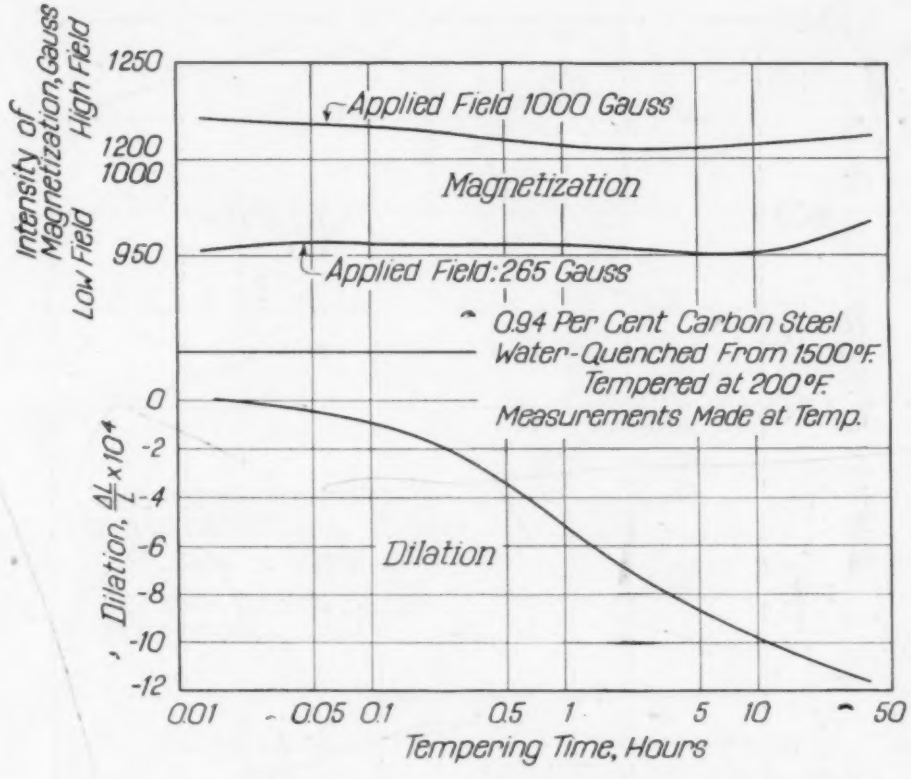


**Fig. 10—Effect of Tempering Time at 200 Degrees Fahr. (95 Degrees Cent.) on the 0.94 Per Cent Carbon Steel After Water Quenching from 1500 Degrees Fahr. (815 Degrees Cent.).**

data for the 0.94 per cent carbon steel. Two marked hardening reactions are observed, one occurring during the early part of the first stage, the other during the second stage. The rapid softening following the second stage is coincident with the third stage.

The results of the X-ray diffraction measurements on the nickel steel are shown in Fig. 6, in which the lattice parameters, the amount of retained austenite and the number of cementite lines are plotted as functions of the tempering temperature. It now becomes obvious that the first stage of tempering involves decomposition of the tetragonal martensite, with the "c" and "a" parameters

becoming identical. The bands indicate the uncertainty in the parameter measurements due to broadening of the observed lines as the tetragonal doublets coalesce into cubic ferrite lines. The tetragonal structure is decomposed long before the second stage is reached. During this first stage, there is no detectable change in either the amount or composition of the austenite. The X-ray intensity determinations demonstrate beyond question that the re-

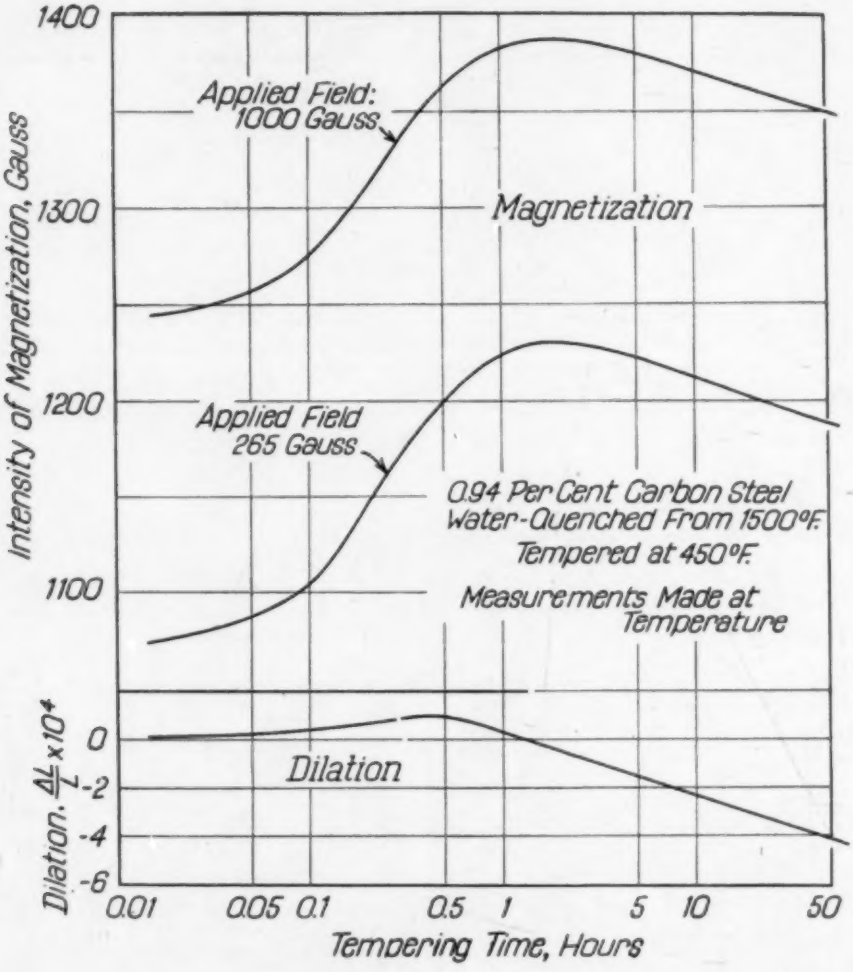


**Fig. 11—Effect of Tempering Time at 450 Degrees Fahr. (230 Degrees Cent.) on the 0.94 Per Cent Carbon Steel After Water Quenching from 1500 Degrees Fahr. (815 Degrees Cent.).**

tained austenite decomposes during the *second* stage, but still without any change in chemistry. Cementite diffraction lines do not appear until the third stage is well under way; thereafter they increase both in number and intensity. At the same time there is a slight decrease in the parameter of the cubic ferrite.

Figs. 7 to 9 illustrate the microstructures of some of the specimens represented by Figs. 5 and 6. After studying Figs. 5 through 9, it becomes evident that the decomposition of tetragonal martensite in the first stage is accompanied by a progressive darkening of the plates (Fig. 7), leaving the retained austenite regions clearly defined. While there is no resolvable structure within the darkened plates, the rapid etching attack is quite suggestive of a

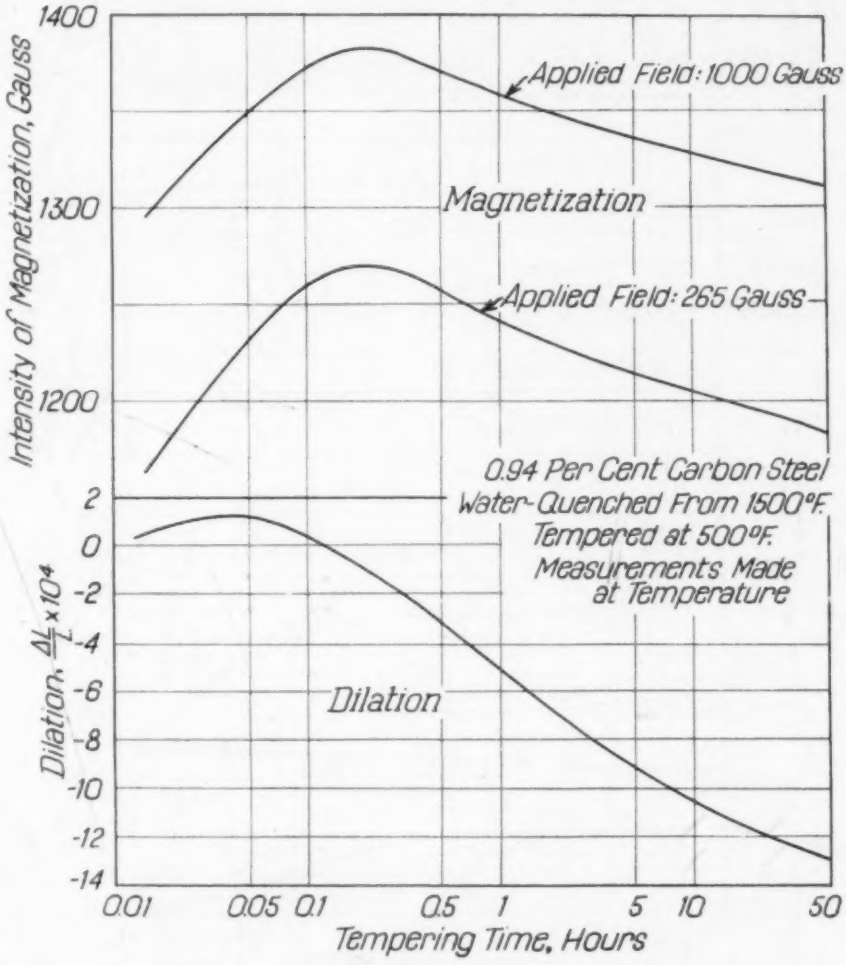


**Fig. 12—Effect of Tempering Time at 500 Degrees Fahr. (260 Degrees Cent.) on the 0.94 Per Cent Carbon Steel After Water Quenching from 1500 Degrees Fahr. (815 Degrees Cent.).**

finely divided precipitate such as commonly appears in age-hardening alloys (33)-(37). The matrix in which this precipitate is embedded is undoubtedly cubic ferrite, whose structure develops from tetragonal martensite as the axial ratio approaches unity. On the other hand, no lines corresponding to the precipitate are observed.

When retained austenite transforms during the second stage (Fig. 8), the product is quite dark-etching, like tempered martensite, and forms very much like bainite, building up angularly from and laterally to the tempered martensite plates. In the latter part of the

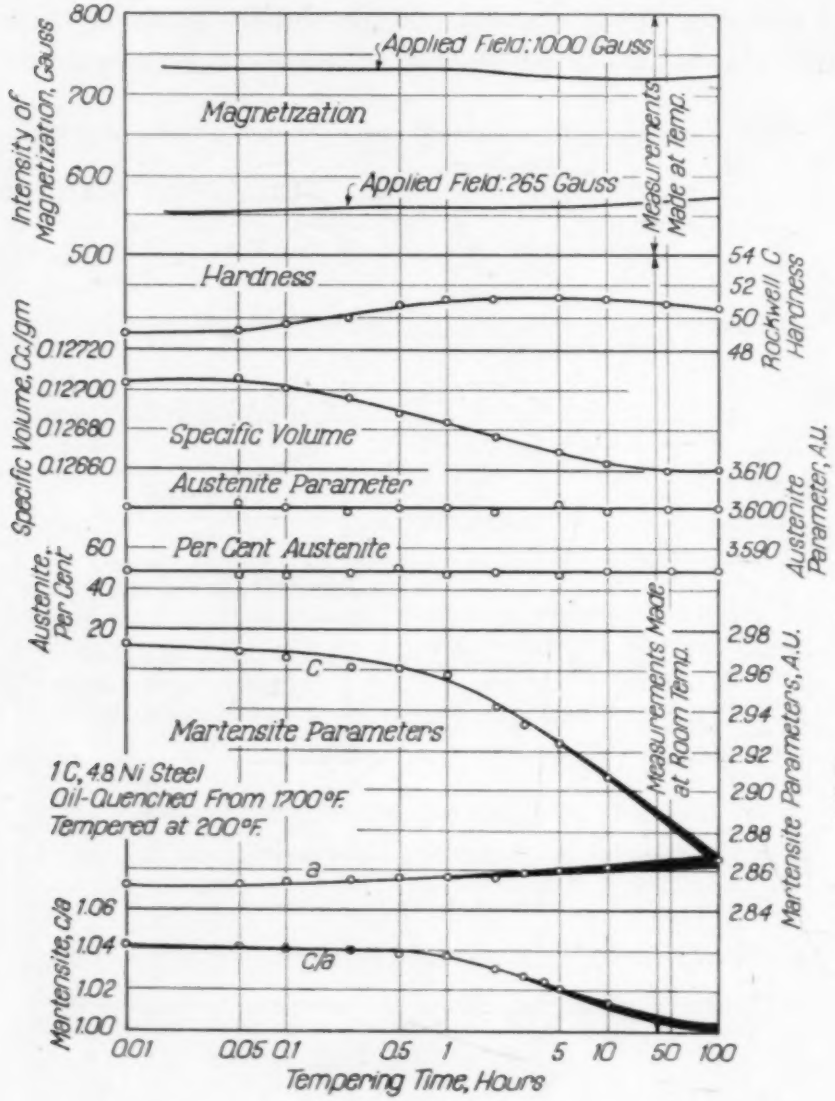


Fig. 13—Effect of Tempering Time at 200 Degrees Fahr. (95 Degrees Cent.) on the Nickel Steel After Oil Quenching from 1700 Degrees Fahr. (925 Degrees Cent.).

second stage (Fig. 8d) and during the third stage (Fig. 9), tiny white precipitate particles gradually become resolvable in both the tempered martensite and the austenite decomposition product.

Frequently the locus of these particles outlines the original configuration of the martensite plates (Fig. 9b). Tempering at

still higher temperatures agglomerates the particles until a typical spheroidized structure is obtained. It is important to note that the cementite lines in the X-ray photograms appear not long after

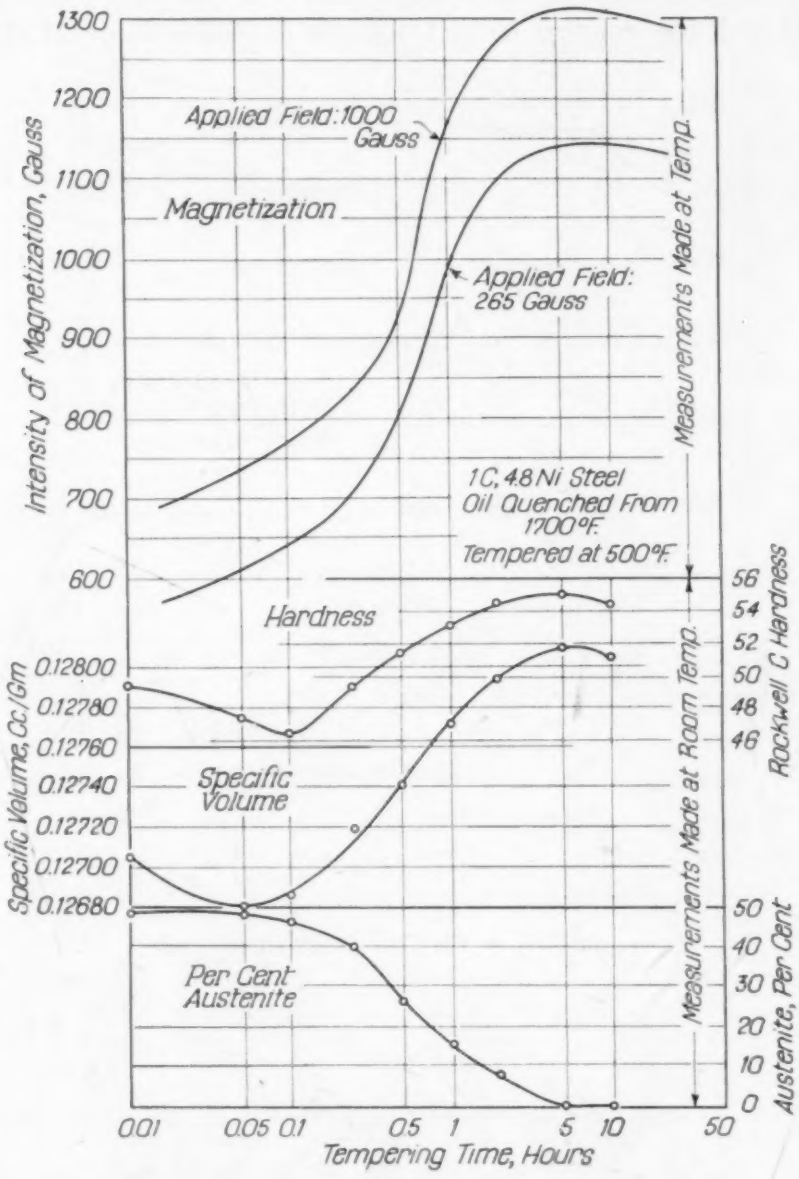


**Fig. 14—Effect of Tempering Time at 500 Degrees Fahr. (260 Degrees Cent.) on the Nickel Steel After Oil Quenching from 1700 Degrees Fahr. (925 Degrees Cent.).**

the emergence of these resolvable particles under the microscope.

While the foregoing results are described in terms of the nickel steel, the same behavior is found in the case of the carbon steel. The microstructures of the carbon steel, however, are not

as clear-cut because of a finer grain size and less retained austenite.

*Isothermal Tempering Runs*—In order to investigate the time dependence of the three tempering reactions, isothermal runs were made at the selected temperatures of 200, 450 and 500 degrees Fahr. (95, 450 and 260 degrees Cent.) for the carbon steel, and 200, 500

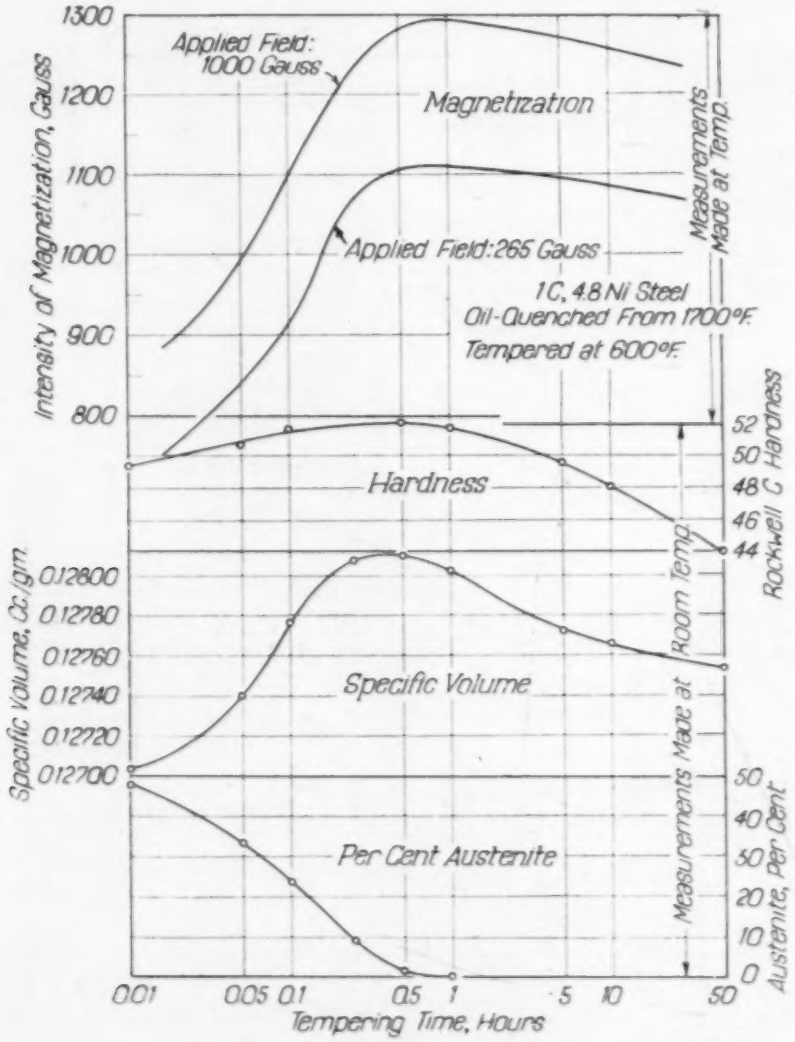


Fig. 15—Effect of Tempering Time at 600 Degrees Fahr. (315 Degrees Cent.) on the Nickel Steel After Oil Quenching from 1700 Degrees Fahr. (925 Degrees Cent.).

and 600 degrees Fahr. (95, 260 and 315 degrees Cent.) for the nickel steel. The results are given in Figs. 10 to 15, and substantiate the survey runs in every way.

At 200 degrees Fahr. (95 degrees Cent.) (Figs. 10 and 13) decomposition of tetragonal martensite proceeds slowly, as shown by

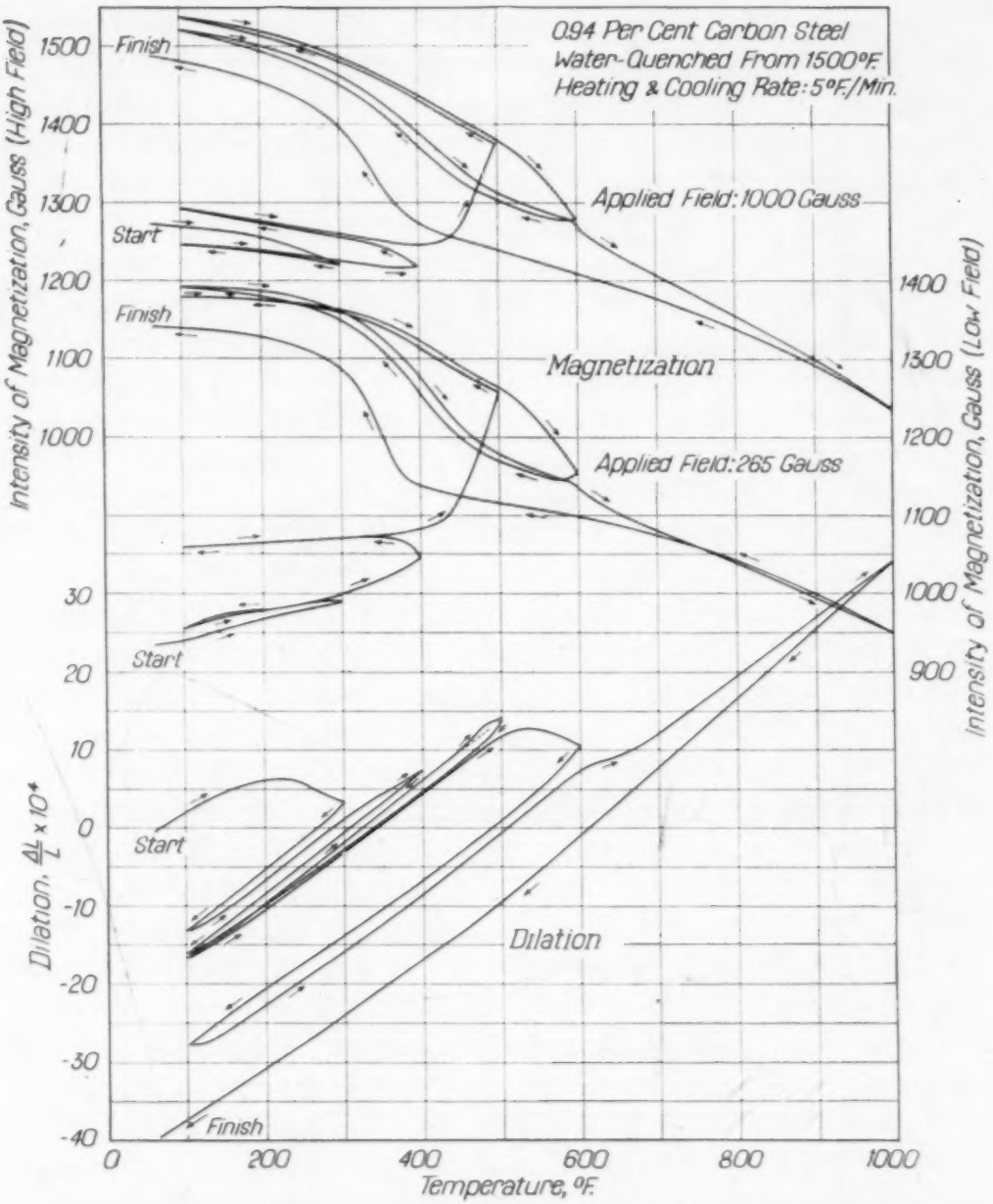


**Fig. 16—Cyclic Magnetization and Dilation Curves for 0.94 Per Cent Carbon Steel After Water Quenching from 1500 Degrees Fahr. (815 Degrees Cent.). Cycles Consist of Heating to and Cooling from 300, 400, 500, 600 and 1000 Degrees Fahr. (150, 205, 260, 315 and 540 Degrees Cent.) Successively at a Rate of 5 Degrees Fahr. Per Minute.**

a gradual decrease in axial ratio and a decrease in both length and volume. The corresponding changes in magnetization are minor, but two trends are detectable. There seems to be an overall tendency for the magnetization to rise slowly on holding at 200 degrees Fahr. (95 degrees Cent.). Since this tendency is more marked at 265 gauss

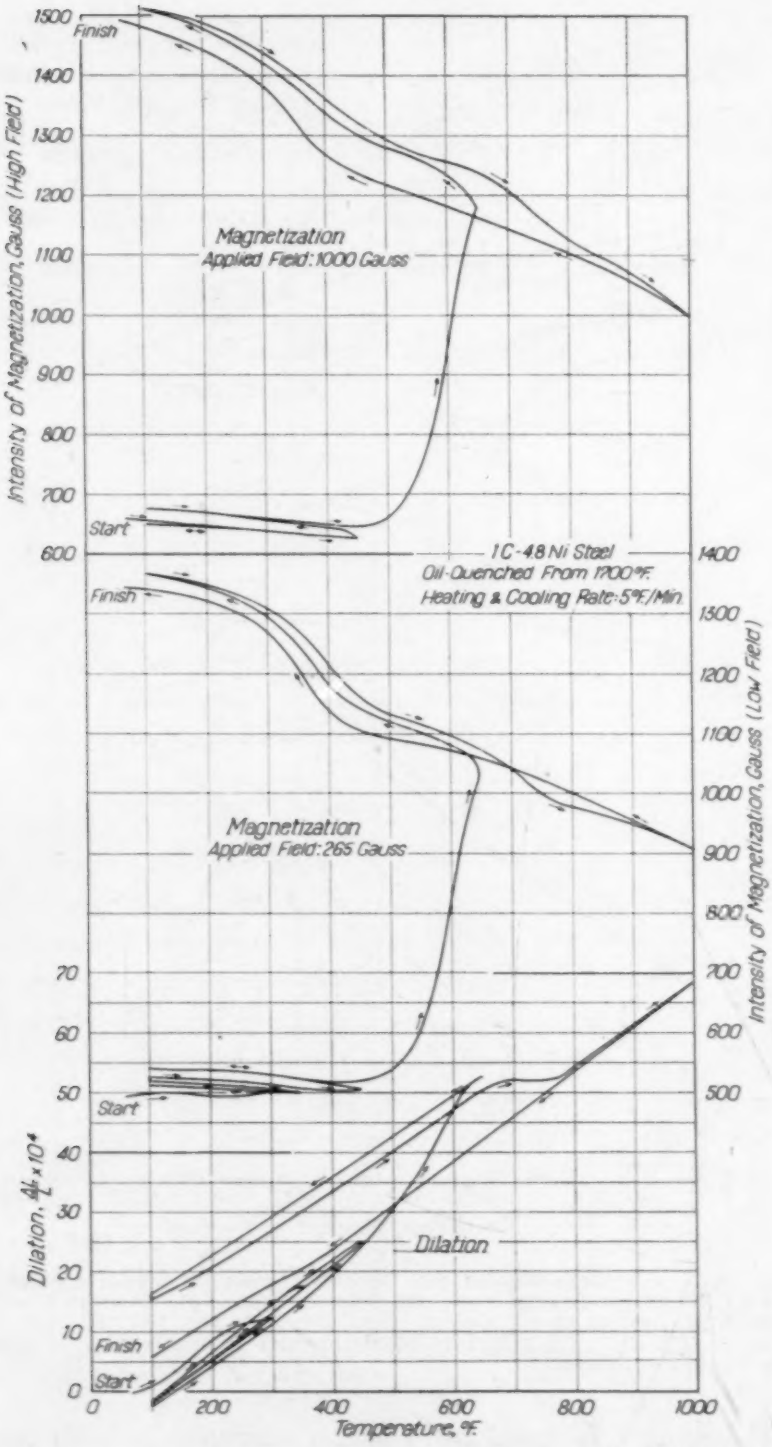


**Fig. 17—Cyclic Magnetization and Dilation Curves for Nickel Steel After Oil Quenching from 1700 Degrees Fahr. (925 Degrees Cent.). Cycles Consist of Heating to and Cooling from 300, 450, 650 and 1000 Degrees Fahr. (150, 230, 345 and 540 Degrees Cent.) Successively at a Rate of 5 Degrees Fahr. Per Minute.**

than at 1000 gauss applied field, it appears that some stress relief goes on at this temperature. However, a barely perceptible decrease in magnetization is superimposed on the stress-relief effect during the time of active martensite decomposition. Consequently, the conclusion may be drawn that the decomposition product is very slightly less ferromagnetic than tetragonal martensite.

The first stage of tempering is complete within a short time at 450 degrees Fahr. (230 degrees Cent.) (carbon steel) and 500 degrees Fahr. (260 degrees Cent.) (nickel steel), and is almost completely masked by the second stage, i.e., the isothermal decomposition of retained austenite (Figs. 11 and 14). In the carbon steel the retained austenite disappears in about 2 hours at 450 degrees Fahr. (230 degrees Cent.), whereas in the nickel steel about 5 hours at 500 degrees Fahr. (260 degrees Cent.) are required. Although the retained austenite decomposition causes distinctive increases in magnetization and dilation, the maxima in these curves do not occur at the same time, even though the measurements are carried out simultaneously on the same specimen (cf. Fig. 11, for example). This apparent anomaly is easily explained: the third stage of tempering sets in before the austenite decomposition is complete, and the decrease in magnetization and length characterizing this stage tends to reverse the effect of the second stage, particularly as it approaches completion. However, the change in length is much more pronounced in the third stage than in the second, while the reverse is true with respect to magnetic changes. Hence, as the third stage gains the ascendancy over the second, the dilation reaches its maximum and begins to decrease before the magnetization does so.

At the higher temperatures of 500 and 600 degrees Fahr. (260 and 315 degrees Cent.) for the carbon and nickel steel respectively (Figs. 12 and 15), the first stage is entirely obscured by the rapid occurrence of the second. The third stage also appears early, and reaches a more advanced state than at the lower temperatures. Cementite diffraction lines appear in the nickel steel after tempering for 24 hours at 600 degrees Fahr. (315 degrees Cent.).

*Cyclic Tempering Runs*—Further information concerning the tempering process may be derived from cyclic magnetic-dilation runs, two of which are shown in Figs. 16 and 17. By following the cooling to room temperature after heating to progressively higher temperatures, it becomes possible to detect the presence of cementite (formed on heating) by the appearance of a Curie point in the magnetic

curves on cooling. Some idea of the sensitivity of this method may be gathered from the fact that an annealed 0.15 per cent carbon steel (2.25 per cent cementite) shows a distinct cementite Curie point. Another advantage of the method is that small cementite particles are reported to produce a more intense magnetic inversion than coarse particles (9); thus the absence of a cementite Curie point cannot be attributed to the fineness of the particles.

No cementite Curie point is found on cooling after the steel has been heated through the first stage, and even after heating well into the second stage. In other words, cementite is not formed in any appreciable quantity when tetragonal martensite and retained austenite first decompose. However, some cementite does form toward the end of the retained austenite transformation, since a slight magnetic inversion appears on subsequent cooling, though at an appreciably higher temperature than usual. As the tempering is carried into the third stage, this Curie point becomes more pronounced and is displaced to lower temperatures, until finally the equilibrium $A_o$ transformation temperature is attained. The same trend is demonstrated in Fig. 18, which shows a family of cooling curves obtained after heating the carbon steel for increasing lengths of time in the third stage at 450 degrees Fahr. (230 degrees Cent.).

## Interpretation of Results

*First Stage of Tempering*—In light of the preceding data, tetragonal martensite transforms into ferrite plus cementite via a two-step process. The first step of martensite decomposition (that is, the first stage of tempering) involves the formation of cubic ferrite and a precipitated phase.* While this precipitate is too finely dispersed to yield a diffraction pattern, it is known to be other than cementite because experiments demonstrate that (a) the precipitate is hardly less ferromagnetic than the martensite, (b) the precipitate does not yield a cementite Curie point, and (c) the contraction accompanying the martensite decomposition is only about one-fourth the calculated value based on the relative densities of martensite, ferrite and cementite (*27*). Furthermore, considering the surprising ease with which tetragonal martensite breaks down on tempering, it is hardly likely that the formation of the complicated cementite structure would be a requisite for this reaction.

*The arguments against the formation of cubic martensite with the carbon atoms still dissolved have already been cited on page 293, and the concept of molecular cementite precipitation has also been refuted on page 294.

It is much more reasonable, and in accord with experimental results, to visualize the precipitate as a transition lattice—an intermediate phase which ultimately develops into cementite during the third stage of tempering. According to several age hardening studies (33)-(37), transition structures are common occurrences in the decomposition of solid solutions; and although they are metastable in a thermodynamic sense, they may persist to appreciably higher temperatures before relaxing into the equilibrium phase. During the first stage of tempering, the transition structure undoubtedly first precipitates in the martensite lattice regions where the statistical carbon concentrations happen to be high; as the tempering time or temperature is increased, regions of lower carbon content undergo precipitation or lose their carbon atoms to the existing precipitate. This results in a gradual lowering of the average carbon concentration in the martensite, and a corresponding loss in tetragonality takes place until the remaining matrix becomes indistinguishable from cubic ferrite. Of course, the above mechanism does not preclude the possible shift of the carbon atoms from the (½, ½, 0) to the (½, ¼, 0) positions in the martensite, as proposed by Honda and Nishiyama (19), but such a shift would be only incidental to the precipitation process.

The formation of a transition precipitate during the first stage of tempering nicely accounts for the darkening of the martensite plates, as well as for the concurrent hardening. Also, in view of the rapidity with which the martensite decomposes, this precipitate might well be expected to contain a higher iron: carbon ratio than corresponds to the cementite composition. This provides at least a qualitative explanation for the more voluminous and magnetic nature of the transition phase as compared to cementite. Even more direct confirmation of a transition lattice forming on martensite tempering has been recently reported in the U. S. S. R. by Arbusow and Kurdjumow (38),* who studied the decomposition of single crystals of martensite. They found new diffraction lines appearing after tempering for 260 hours at 265 degrees Fahr. (130 degrees Cent.), and finally detected five such lines not belonging to any of the usual phases. Moreover, on tempering above 570 degrees Fahr. (300 degrees Cent.) these lines disappeared in favor of cementite lines. This is very convincing evidence of a transition structure. However, it must be stated that these new lines were not observed in the present work, or in any other published research dealing with polycrystalline

*This paper was received after completion of the present work.

martensite. Presumably, the single-crystal technique is more capable of revealing the presence of a dispersed precipitate.

*Second Stage of Tempering*—It is quite certain that the retained austenite transforms during the second stage of tempering. Especially conclusive evidence is provided by the measured decrease in intensity of the austenite diffraction lines which takes place at that time. In the steels examined this transformation may occur either isothermally or on heating, and is not preceded or accompanied by a change in carbon content (as shown by the constancy of the austenite lattice

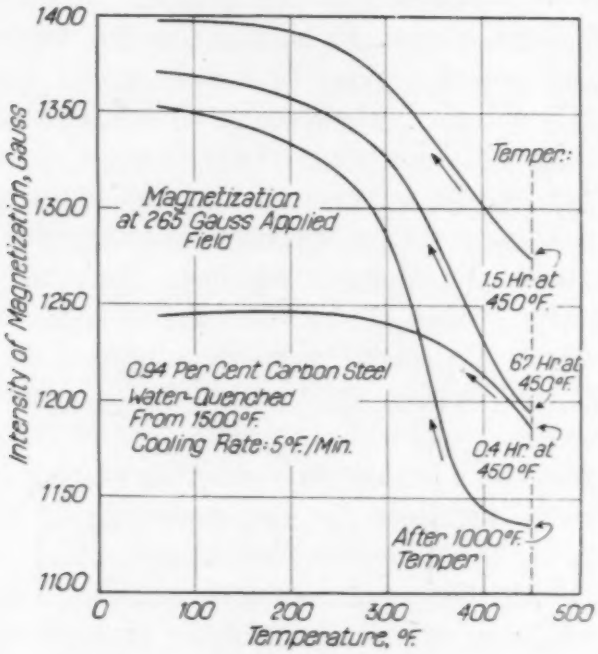


**Fig. 18—Magnetization Curves on Cooling the 0.94 Per Cent Carbon Steel After Tempering for Various Times at 450 Degrees Fahr. (230 Degrees Cent.).**

parameter during its decomposition). Since a cementite Curie point is not observed until after the bulk of the austenite decomposes, the initial product cannot be regarded as a ferrite-cementite mixture. In fact, the indications are that the product is quite similar in state of aggregation to the dark-etching tempered martensite. In general appearance under the microscope, however, its acicular configuration is more like bainite.

Because of gradual softening of tempered martensite, and perhaps even more because of relief of stresses, the hardness starts to decrease long before the second stage of tempering is reached. The latter reaction, however, tends to retard this softening, or even

causes secondary hardening if enough retained austenite is originally present.

The one-time view that retained austenite in carbon steels transforms momentarily to martensite (1) before forming an aggregate is open to serious question. In the first place, the martensite-formation range with respect to *retained* austenite is below room temperature. In the second place, the austenite-martensite transformation occurs characteristically on cooling, and there has been no indication in this work that any such transformation with respect to retained austenite is encountered on cooling after tempering. In the third place, the temperatures at which retained austenite decomposes are well above the range at which martensite can exist. Consideration of these facts leads to the conviction that retained austenite must transform directly into an aggregate without passing through the martensite state.

*Third Stage of Tempering*—The appearance of a cementite Curie point toward the latter part of the second stage is a manifestation of the third stage setting in with the formation of cementite. Somewhat less sensitive to the presence of cementite, but an even more positive indication, is emergence of the cementite diffraction pattern during the third stage. The microstructure shows that the cementite particles develop and grow out of the martensite and austenite decomposition products of the first and second stages, respectively, until a typical spheroidized structure ultimately is formed. In other words, the transition structure precipitated with ferrite from martensite and austenite persists over a considerable range of temperatures before transforming into cementite. Evidently, as in the case of other transition precipitates, there is a high degree of coherency or lattice registry with the matrix, and additional atomic mobility must be attained before the precipitate can break away from the matrix and adopt the more stable cementite structure. Diffusion is also required to enable the precipitate to acquire the proper complement of carbon atoms characteristic of cementite. The slight decrease in lattice parameter of the ferrite matrix in this range denotes the drawing of dissolved carbon from the ferrite. Rapid softening occurs during the cementite-formation stage, probably brought about by agglomeration and by the relaxation of stresses which previously maintained lattice coherency between the matrix and the transition precipitate (36), (37). Unquestionably, the cementite first formed is not perfect in structure nor stoichiometric in composition. The progressive lowering and intensification of the cementite Curie point as the

tempering proceeds in the third stage (Fig. 18) testify to the gradual achievement of a normal cementite phase.

The large drop in magnetization which takes place during the third stage also fits into the picture. Since the transition precipitate is highly magnetic up to the temperatures at which it becomes converted, and since the cementite formed thereby is paramagnetic (being above its Curie point), a substantial decrease in magnetization would be expected to accompany this conversion. Even at room temperature, where cementite is quite ferromagnetic, the transition pre-

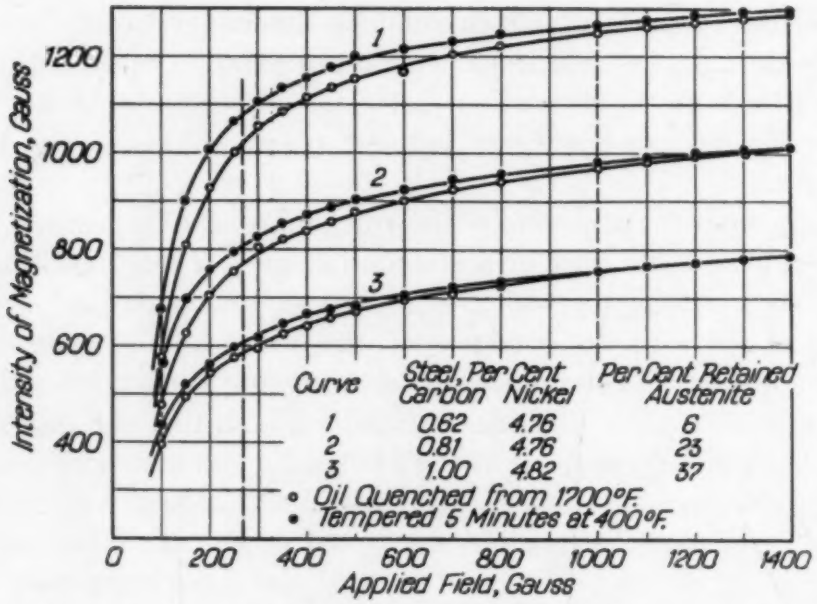


Fig. 19—Magnetization Curves as Measured at Room Temperature for Three 4.8 Per Cent Nickel Steels After Oil Quenching from 1700 Degrees Fahr. (925 Degrees Cent.) and After Tempering at 400 Degrees Fahr. (205 Degrees Cent.) for 5 Minutes. Note the Gaps Between Each Curve of a Pair at 265 Gauss as Compared to 1000 Gauss.

cipitate is still more magnetic. This is demonstrated in Figs. 16 and 17, in which the room temperature magnetization values are higher after the second stage of tempering (i.e., after the retained austenite has been decomposed but not much of the transition phase has been converted to cementite) than after the third stage in which complete cementite formation has been attained.

While agglomeration of cementite particles occurs during, as well as after, the third stage of tempering, it must be emphasized that the observed magnetic, X-ray diffraction and volumetric phenomena cannot possibly be explained on this simple basis. The fundamental essence of the third stage is *cementite formation.*

*Stress Relief*—As previously mentioned, magnetic changes at the low applied field of 265 gauss suggest that stress relief accompanies the tempering process. This effect is particularly apparent between the first and second stages where the phase reactions are of a minor order. On heating through this temperature range of 320 to 450 degrees Fahr. (160 to 230 degrees Cent.) (cf. Fig. 1), the magnetization at very high fields undergoes a decrease, as expected from the normal temperature coefficient. At the lower fields, however, the slope gradually becomes less negative, and is actually decidedly positive at 265 gauss.

Further light is shed on this phenomenon by the cyclic curves in Fig. 16, where the heating is interrupted at 300 degrees Fahr. (150 degrees Cent.) and at 400 degrees Fahr. (205 degrees Cent.) by coolings to room temperature. It is evident that the slope of the magnetic curve as measured at 265 gauss becomes less positive as a result of these heatings, while the slope of the high field curve is equally negative before and after these cycles. Such effects as these are not typical of phase changes, but are logically attributable to stress relief.

It will be observed that the stress-relief effect is not so pronounced in the magnetic curves for the nickel steel (Fig. 4) as for the carbon steel (Fig. 2). This difference is entirely in accord with the above reasoning, for the nickel steel, cooled at a slower rate and forming less martensite during quenching, would be expected to have a considerably lower stress level, and therefore undergo less stress relief on tempering.

However, even the nickel steel displays signs of stress relief when the magnetization curves are measured at room temperature before and after suitable tempering. Fig. 19 shows such curves for 4.8 per cent nickel steels with 0.6, 0.8 and 1.0 per cent carbon and 6, 23 and 37 per cent retained austenite respectively. In each case, tempering at 400 degrees Fahr. (205 degrees Cent.) for 5 minutes produces no austenite decomposition, but does cause an increase in magnetization at low fields, and this increase gradually disappears as the field strength is raised. Moreover, the spread between each pair of curves at low fields becomes less with increasing amounts of retained austenite in the hardened structure. Obviously, the hardening stresses, and the subsequent stress relief on tempering, diminish in magnitude as more and more austenite is retained.

According to Fig. 5, rapid softening takes place between the

first and second stages of tempering, both of which are hardening reactions. Inasmuch as there is relatively little structural change going on through this range, much of this softening is undoubtedly caused by the relief of stresses.

## Conclusions

1. High carbon steel, whether of high purity or of commercial grade, undergoes three pronounced stages during tempering.
2. The first of these stages is caused by the decomposition of the tetragonal martensite into an aggregate consisting of ferrite and a transition precipitate. This precipitate is not cementite, but ultimately transforms into cementite during the third stage of tempering.
3. The second stage is characterized by the decomposition of the retained austenite into an acicular product having the same state of aggregation as the tempered martensite.
4. The third stage is caused by the genesis and development of cementite from the transition precipitate formed during the first two stages. Agglomeration of the cementite particles takes place during, as well as after, the third stage until a typical spheroidized structure is attained.
5. All the tempering reactions are time-dependent, occurring at lower temperatures with longer tempering times.
6. There is evidence of stress relief overlapping the three tempering stages.
7. These tempering effects are consistent with the observed changes in magnetization, dilation, specific volume, hardness, microstructure and X-ray diffraction.

## Acknowledgments

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## DISCUSSION

**Written Discussion:** By Otto Zmeskal, research metallurgist, Universal-Cyclops Steel Corp., Bridgeville, Pa.

In the opinion of the writer, this work is destined to stand as one of the classic papers presented to this Society. One of the outstanding contributions of this paper is the clarification of the martensite tempering reaction. It is now an indisputable fact that martensite tempers to ferrite and a transition phase that is not cementite. Furthermore, the authors have shown that no precipitation occurs

from the retained austenite prior to its transformation to an acicular structure during heating. What is the austenite transformation mechanism? The previous explanation was that carbide precipitated from the austenite, and so conditioned it for transformation. The writer would like to ask for a clarification of this point.

In reference to the magnetic measurements conducted by the authors, it is interesting to note that the intensity of the Curie point effect is greater when the measurement is made at the lower applied field of 265 gauss. In the future, no doubt the number and types of measurements that will be used to study heat treatment kinetics, will be wide and varied, but the writer does not believe that the fundamental mechanisms presented in this paper will be altered.

**Written Discussion:** By George Freedman, plant metallurgist, Raytheon Production Corp., Newton, Mass., and Sidney Siegel, metallurgist, Naval Research Laboratory, Washington, D. C.

In an investigation at the Massachusetts Institute of Technology, the authors measured changes in resistivity of 0.79 per cent carbon commercial steel during tempering from room temperature to 1000 degrees Fahr. (540 degrees Cent.), after

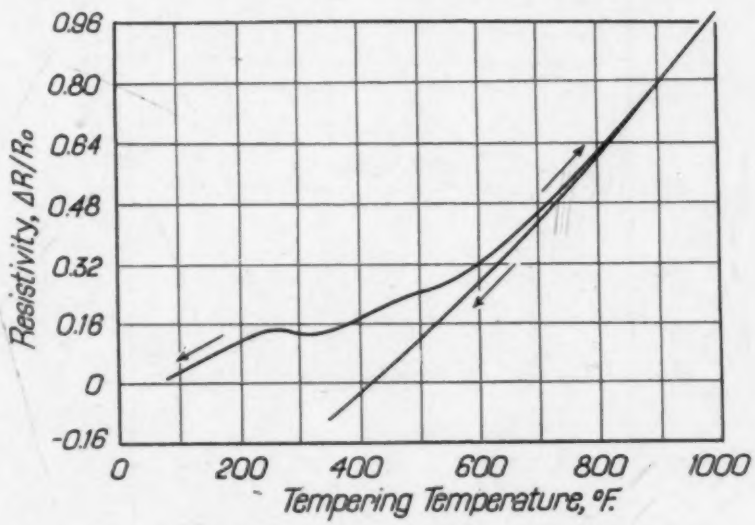


**Fig. A—Variation of Electrical Resistivity with Tempering Temperature.**

water quenching from 1575 degrees Fahr. (855 degrees Cent.). Heating rate during tempering was 5 degrees Fahr. per minute. Change in resistivity is plotted as $\Delta$ R/Ro, Ro being the resistance of the steel specimen at room temperature and $\Delta$ R being the increment between the resistance at any temperature and the resistance at room temperature. This method of plotting makes it possible to compare the results of different sizes of specimens directly. The resistivity curve (Fig. A) shows excellent agreement with the curves of the paper under discussion. The lower carbon content used in this investigation has decreased the relative intensity of variations due to the tempering reactions in comparison with the size of the discontinuities in the dilation curves of the paper. However, the three tempering stages occur unmistakably and at closely the temperatures indicated by the paper.

**Written Discussion:** By Robert T. Howard, assistant, department of metallurgy, Massachusetts Institute of Technology, Cambridge, Mass.

The authors have contributed a valuable addition to the literature on the tempering of carbon steels. They have found certain definite stages of tempering which heretofore have been only hazily described. The discusser recently had occasion to conduct a series of magnetic measurements on high carbon steels, and was able to substantiate the authors' conclusions.

The steels used were commercial plain carbon grades containing 0.70 and 1.26 per cent carbon. Rod-shaped specimens (4.25 inches long by 0.25 inch diameter) were first hardened by quenching in high speed oil after being austenitized at 1500 and 1800 degrees Fahr. (815 and 980 degrees Cent.) respectively.

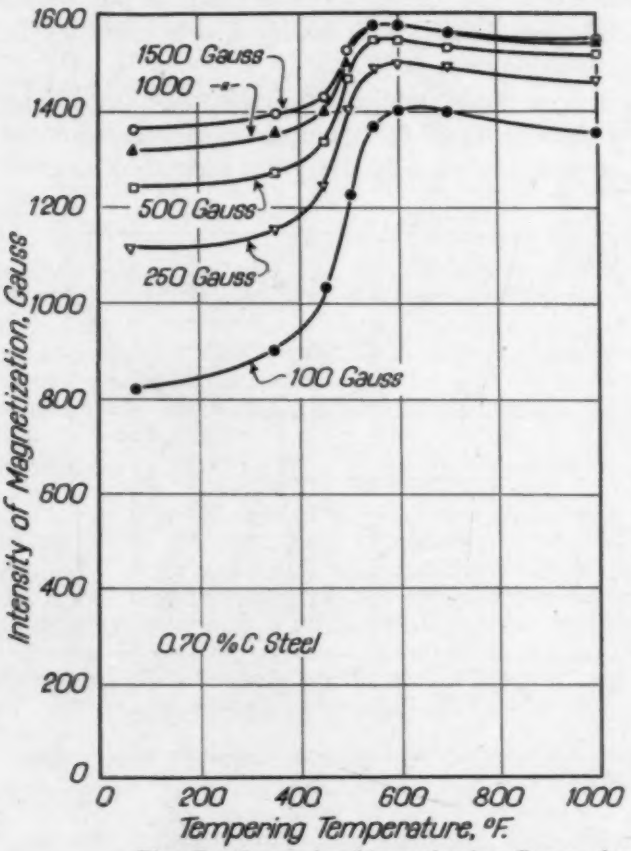


Fig. B—Tempering-Magnetization Curves for a 0.70 Per Cent Carbon Steel Quenched from 1500 Degrees Fahr.

These specimens were then tempered for 5-minute intervals at successively higher temperatures, commencing at 300 degrees Fahr. (150 degrees Cent.). The heating was carried out in salt to assure rapid temperature equalization. After each 5-minute temper, the specimens were cooled in air to room temperature for magnetic measurements. Complete magnetization curves such as appear in figures of the authors' paper were obtained after each temper. However, for the purpose of this discussion, the magnetic intensity data are plotted as a function of the tempering temperature for selected fields of 100, 250, 500, 1000 and 1500 gauss. (Figs. B and C.)

The plots so obtained bear out the authors' hypotheses. The first stage of tempering, characterized by the decomposition of the tetragonal martensite with accompanying stress relief, is strikingly demonstrated in the curves for the 0.70 per cent carbon steel in Fig. B. Here, in the 300 to 400 degrees Fahr. (150 to 205 degrees Cent.) range, the magnetization increases markedly at low field strengths, but much less so at the higher fields. In the case of the 1.26 per cent carbon steel, there is less martensite because there is more retained austenite, and the stress effect is less evident.

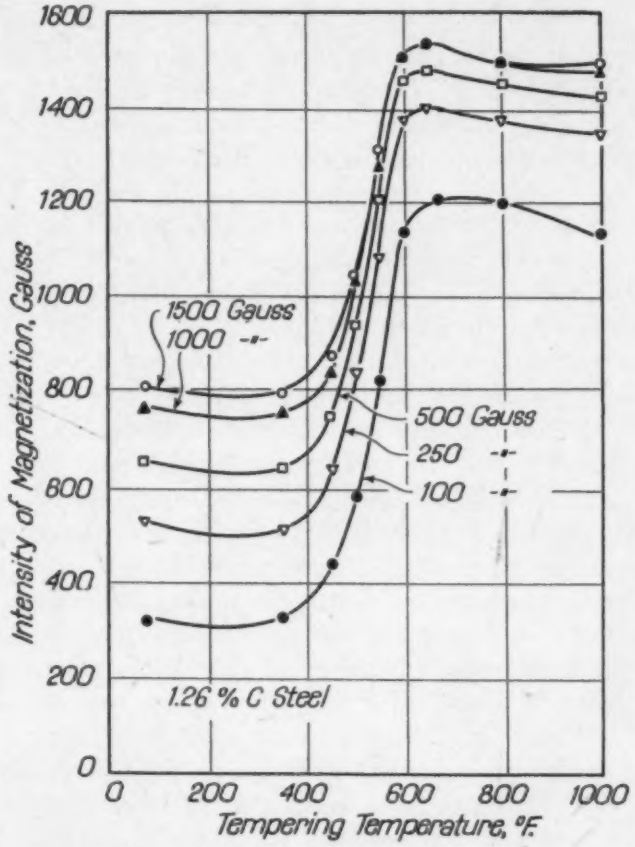


Fig. C—Tempering-Magnetization Curves for a 1.26 Per Cent Carbon Steel Quenched from 1800 Degrees Fahr.

The large increase in magnetization at 450 to 600 degrees Fahr. (230 to 315 degrees Cent.), due to the transformation of the retained austenite, is the signal feature of these curves. This phenomenon is the same for both steels, except that the increase in magnetization is more pronounced and the effect persists to higher temperatures in the case of the 1.26 per cent carbon steel. This is attributable to the presence of more retained austenite in the latter steel.

Perhaps the most important aspect of Figs. B and C is the substantiation of the authors' belief concerning the third stage of tempering. According to their postulate, the precipitation and coalescence of carbides from the transformation products of tetragonal martensite and retained austenite in the 500 to 650 degrees Fahr. (260 to 345 degrees Cent.) range should tie-up a considerable amount of

iron as cementite ($Fe_3C$) which is less magnetic than ferrite. Hence there should be a noticeable decrease in the room temperature magnetization as a result of heating through the third stage. This picture is verified by the curves presented since there is a definite decrease in magnetization beyond the peak values in the 550 to 600 degrees Fahr. (290 to 315 degrees Cent.) range. It is significant that, while the magnitude of the decrease is the same for each steel, the ultimate as well as the peak magnetization values are less for the 1.26 per cent carbon steel. This may be explained by the larger amount of carbon and consequently cementite in the 1.26 per cent carbon steel. The overlapping of stages two and three indicates that the greater decrease in magnetization expected in the 1.26 per cent carbon steel due to the precipitation of carbides is obscured by the continuing increase in magnetization of the transforming austenite. Therefore, the ultimate magnetization of the completely transformed steels offers a better picture of the amount of carbide precipitation than does the magnitude of the decrease from the peak values.

These results appended to the authors' contribution should lend farther weight to their picture of the tempering process.

**Written Discussion:** By Charles S. Barrett and Elizabeth Saffer, Carnegie Institute of Technology, Pittsburgh, Pa.

The electron microscope should be added to the extensive list of methods by which the authors have studied the tempering of martensite. The authors kindly furnished us the samples they had used for the photomicrographs of their paper so the same structures could be investigated by this new tool. Representative nickel steel samples were repolished and etched, and polystyrene-silica replicas were prepared and viewed under the R C A microscope at Carnegie Tech. Typical results are reproduced in the following micrographs.

The first three electron micrographs were made after etching with nital. Fig. D shows the specimen of 1.0 per cent carbon, 4.8 per cent nickel steel tempered 5 minutes at 350 degrees Fahr. (175 degrees Cent.). The structure consists of tetragonal martensite in a matrix of austenite (49 per cent by volume) and has a hardness of 51 Rockwell C. The nital has attacked the surface of the martensite at many closely spaced points about 0.1 micron apart, but has left the austenite relatively unetched. The roughened surface of the martensite here shown accounts for the darkening of the needles in the optical microscope.

Fig. E is the same steel tempered 5 minutes at 550 degrees Fahr. (290 degrees Cent.), with 25 per cent austenite and with martensite that has been tempered to the cubic form. Here the nital has dug deeper and coarser pits in the martensite. There is some evidence of alignment of pits into rows.

Fig. F shows the result of tempering at 700 degrees Fahr. (370 degrees Cent.). The hardness is 48 Rc, and the structure contains only cubic tempered martensite with no austenite. The eching has produced grooves in an acicular pattern over the entire surface. No cementite particles can be identified.

The last four electron micrographs illustrate picral etching on the same samples. The specimen tempered at 350 degrees Fahr. (175 degrees Cent.), Fig. G, is almost completely acicular, and appears so under the optical microscope also. This suggests that austenite decomposition has been preceding at room temperature during the two years since it was heat treated.

Fig. H is another area on this specimen, and here are seen plates of tempered

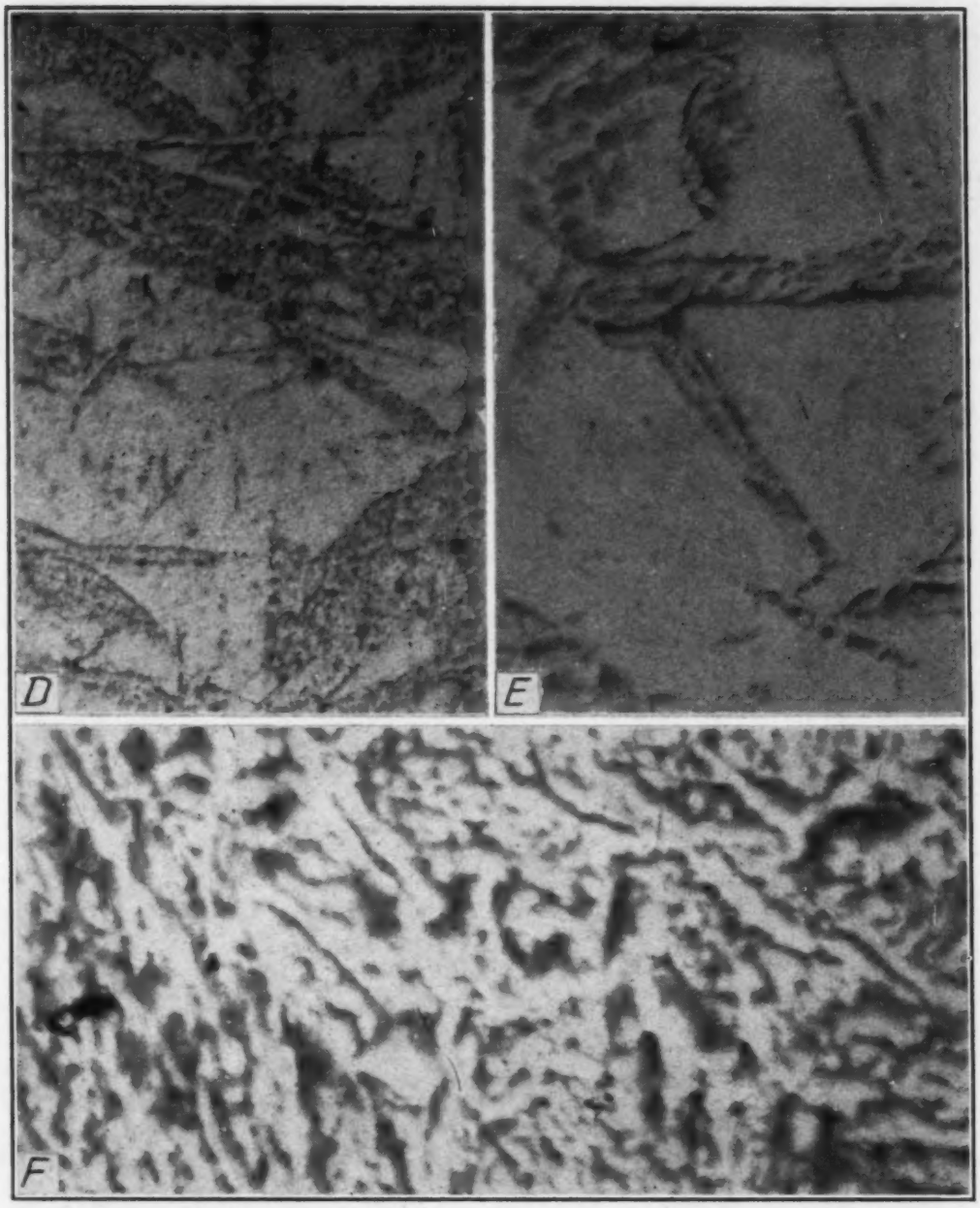


Fig. D—Photomicrograph of Specimen of 1.0 Per Cent Carbon, 4.8 Per Cent Nickel Steel Tempered 5 Minutes at 350 Degrees Fahr. Nital Etch. × 8000.

Fig. E—Same Steel as Fig. D, Tempered 5 Minutes at 550 Degrees Fahr. Nital Etch. × 8000.

Fig. F—Photomicrograph Showing the Result of Tempering at 700 Degrees Fahr. Nital Etch. × 8000.

martensite that appear to be embedded in austenite.

Fig. I shows the sample tempered at 550 degrees Fahr. (290 degrees Cent.). The black dots, which are isolated dots in this area, are sometimes found to be connected with a network of grooves, but acicular markings are rare with this etchant and this sample.

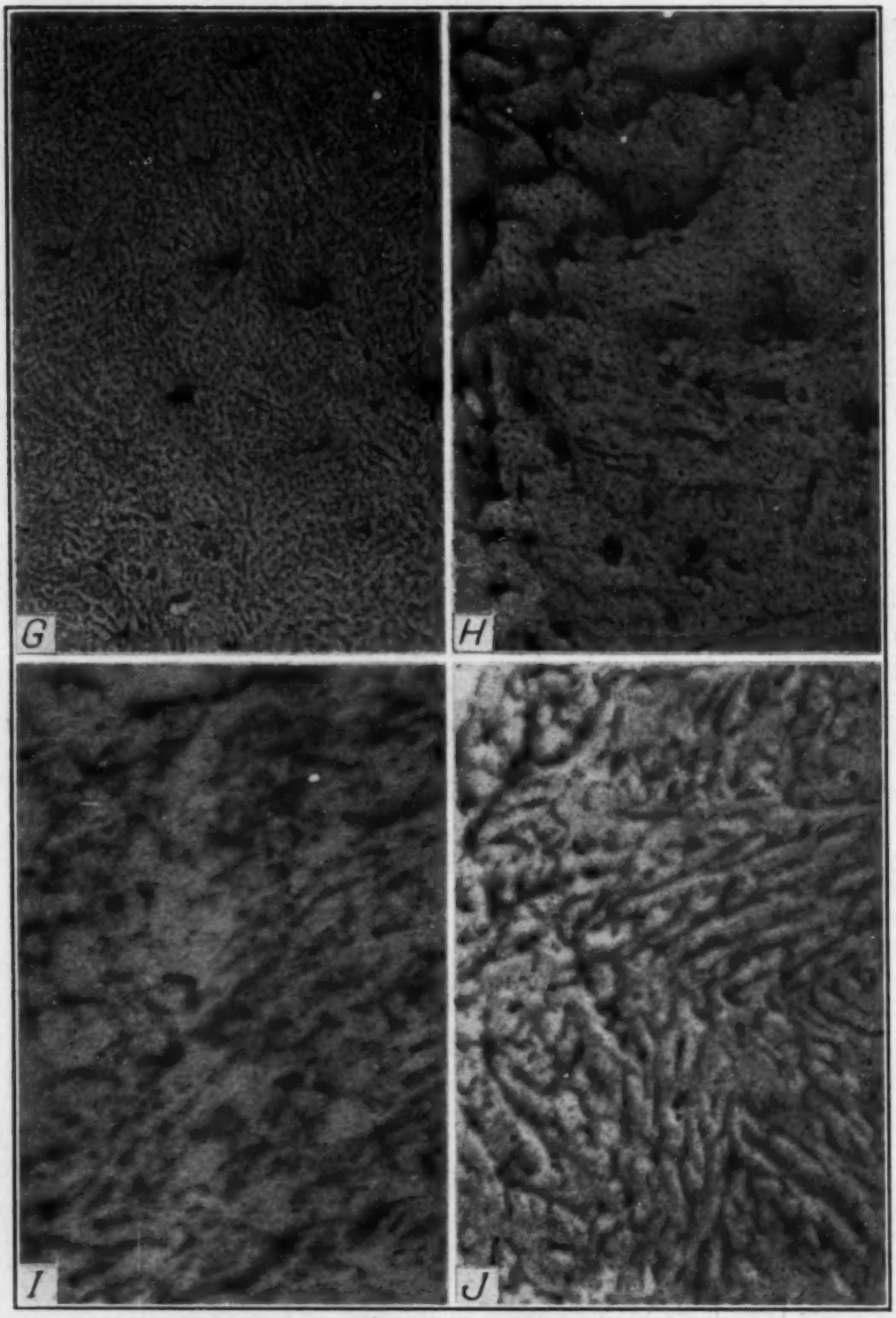


Fig. G—Photomicrograph of Same Samples as Figs. D, E and F. Tempered at 350 Degrees Fahr. Picral Etch. × 8000.

Fig. H—Photomicrograph of Another Area of Same Specimen. Tempered at 350 Degrees Fah. Picral Etch. × 8000.

Fig. I—Photomicrograph of Same Sample Tempered at 550 Degrees Fahr. iP cral Etch. × 8000.

Fig. J—Photomicrograph of Same Structure Tempered at 700 Degrees Fahr. Picral Etch. × 8000.

Fig. J represents the structure after 700 degrees Fahr. (370 degrees Cent.) tempering, which resembles very closely the structure produced in this sample by etching in nital.

From the series as a whole, it appears that the principal microscopic change during the tempering of martensite is an increase in the dimensions of the etch pits as the temperature of tempering is raised, together, of course, with a decrease in the amount of austenite. The coarsening of the etch pits probably signifies a coarsening of the precipitate and closely resembles the coarsening seen in electron micrographs of an age hardening alloy when it is overaged.[1] Too little is known about the fine-scale action of acids on polished metals to deduce much regarding a transition precipitate, from these pictures, or to judge the exact size or shape of cementite particles.

## Authors' Reply

We are glad to receive the comments of our former colleague, Dr. Zmeskal, who was largely responsible for the design and construction of the combined magnetometer-dilatometer that we have been using so extensively in our tempering studies. He points out, and rightly so, that the Curie point inversion appears more clearly at 265 gauss than at 1000 gauss. The greater sensitivity of the low field measurements in this connection is of particular significance in carbide studies designed to follow slight changes in composition.

The mechanism of austenite decomposition to which Dr. Zmeskal refers is applicable to high speed steel and other highly alloyed steels in which the retained austenite is quite sluggish. In such cases, the retained austenite does not decompose isothermally to any considerable extent during normal tempering; instead, the chemistry of the retained austenite changes because of carbide precipitation until martensite formation becomes possible on cooling back to room temperature. In straight carbon and low alloy steels, however, the retained austenite is much less stable, and undergoes isothermal decomposition into bainite or into ferrite-carbide aggregates depending on the tempering temperature. It has been emphasized elsewhere[2] that the cooling and the isothermal modes of retained austenite transformation are not mutually incompatible. Both types occur in high-carbon, high-chromium steels[3] where retained austenite of intermediate stability is obtainable. Presumably, even the retained austenite in plain carbon steels would transform into martensite on cooling from the tempering treatment if it were not for the fact that the austenite decomposes isothermally before enough carbide precipitation can take place to alter its chemistry appreciably.

We are pleased to find that the electrical resistance measurements of Messrs. Freedman and Siegel confirm the three basic stages of tempering. It is interesting to note that each stage is accompanied by a decrease in resistance (which, of course, is superimposed on the temperature-dependent resistance changes). Of especial importance is the fact that the temperature coefficient of resistance seems

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[1]C. S. Barrett, T. P. 1637, *Metals Technology*, Sept., 1943.

[2]D. P. Antia and M. Cohen, "The Tempering of Nickel and Nickel-Molybdenum Steel," TRANSACTIONS, American Society for Metals, Vol. 32, 1944, p. 363.

[3]O. Zmeskal and M. Cohen, "The Tempering of Two High-Carbon High-Chromium Steels," TRANSACTIONS, American Society for Metals, Vol. 31, 1943, p. 380.

to be abnormally small over the temperature range between the first and second stages. This phenomenon is easily explained by the stress relieving process which has been indicated independently by magnetic and hardness measurements.

Mr. Howard's *room temperature* magnetization curves are most interesting when compared with the *at temperature* magnetization curves shown by the authors. The stress relief and austenite decomposition effects are quite clear in both cases, but the room temperature observations disclose only a small decrease in magnetization for the third stage. This is because the cementite formed during the third stage is ferromagnetic at room temperature, but is paramagnetic at its formation temperature.

The electron microscope studies contributed by Dr. Barrett and Miss Saffer are greatly appreciated. Their micrographs seem to fit into the tempering picture presented in this paper, but we must confess that it would be difficult to interpret these electron microstructures if the state of the specimens were not otherwise known. We are in agreement with the comments of the discussers, except possibly on two points. (1) There appears to be a myriad of indistinct white spots in Fig. F which conceivably could be cementite particles. The change in these spots with further tempering should be followed in order to ascertain their significance. (2) We doubt that there could have been sufficient room temperature decomposition of the retained austenite to account for its non-appearance in Fig. G. Either the area photographed was not representative or it was not selectively etched by the picral. Both Fig. H and Fig. D taken on the same specimen (tempered 5 minutes at 350 degrees Fahr.) demonstrate that large quantities of retained austenite are actually present. It is hoped that Dr. Barrett and his coworkers will continue their electron micrographic studies of tempered structures.

# THE EFFECT OF CARBON ON THE TEMPERING OF STEEL

By Stewart G. Fletcher and Morris Cohen

*Abstract*

*The effects of carbon content on the tempering characteristics of plain carbon steels are studied by means of magnetic, dilatometric, X-ray diffraction and hardness measurements. This investigation is confined to steels and high-purity iron-carbon alloys which have been heat treated so that only tetragonal martensite and retained austenite exist in the structure prior to tempering. The retained austenite contents after hardening are determined by a specific volume method, and are found to increase rapidly with the per cent of carbon. For a given carbon content, the high-purity alloy retains less austenite than the corresponding steel.*

*All the steels exhibit the three fundamental stages of tempering previously reported, but in varying degree. Carbon appears to have little effect on the temperature ranges over which these stages occur, and on the rates of reaction within each stage. However, the property changes associated with each stage of tempering become intensified as the carbon content increases, provided that account is taken of the amount of martensite or austenite participating in the transformation.*

*Extensive hardness data indicate that the first stage (tempering of martensite) is a hardening reaction, increasing in magnitude with increasing carbon content. While the decomposition of retained austenite (second stage) is also a hardening transformation, the secondary hardening thus produced becomes pronounced only when more than 20 per cent austenite is initially present. The third stage (formation and growth of cementite) results in marked softening.*

*Calculations, based on dilatometric and lattice parameter data, demonstrate that cementite is not formed*

This paper is based in part on a thesis submitted by Stewart G. Fletcher to the Department of Metallurgy, Massachusetts Institute of Technology, in partial fulfillment of the requirements for the degree of Doctor of Science.

A paper presented before the Twenty-fifth Annual Convention of the Society, held in Chicago, October 18 to 22, 1943. Of the authors, Stewart G. Fletcher is research assistant, and Morris Cohen is associate professor of metallurgy at the Massachusetts Institute of Technology, Cambridge, Mass. Manuscript received July 19, 1943.

*to any appreciable extent during the initial tempering of martensite (first stage); however, there are strong indications that a transition structure precipitates during this transformation. Other computations have been made to ascertain the specific volume of tempered martensite, and to separate the volumetric effects of the second and third stages of tempering, which normally overlap. All these calculations confirm that increasing carbon content brings about intensification of the changes on tempering.*

## Introduction

RECENT studies (1, 2)[1] have shown that high carbon steels undergo three distinct transformations during tempering, the cumulative effect of which is a conversion of tetragonal martensite and retained austenite into ferrite and cementite. These structural changes take place in the following sequence:

(A) First stage—about 180 to 320 degrees Fahr. (80 to 160 degrees Cent.)—precipitation of a transition structure from the tetragonal martensite, reducing the latter to cubic ferrite.[2]

(B) Second stage—about 450 to 540 degrees Fahr. (230 to 280 degrees Cent.)—decomposition of the retained austenite into a bainite-like product, similar in state of aggregation to the tempered martensite.

(C) Third stage—about 500 to 675 degrees Fahr. (260 to 360 degrees Cent.)—formation and growth of cementite from the transition structure precipitated during the first and second stages.

The present paper is concerned primarily with the effect of carbon content on the nature and magnitude of these three stages of tempering.

## General Experimental Methods

*Materials Used* — The measurements reported here were made on four commercial plain carbon steels and three high-purity iron-carbon alloys, the analyses of which are given in Table I.

The commercial steels were purchased in the form of rods

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

[2]This aggregate of cubic ferrite and the transition precipitate will hereinafter be referred to as "tempered martensite."

up to 0.75 inch in diameter, and were machined to 0.240-inch rounds for the experimental work. On the other hand, the high-purity iron-carbon alloys were prepared in a laboratory induction furnace from electrolytic iron and graphite, melted and chill-cast in a vacuum as 5.5-pound ingots. After an homogenizing anneal at 1800 degrees Fahr. (980 degrees Cent.), the ingots were forged to half-inch stock from which 0.240-inch rounds were machined. All surface defects and decarburization were thus removed.

**Table I**
**Chemical Analyses**

| Designation | Material | Per Cent by Weight | | | | | | Austenitizing Temperature Degrees Fahr. | Quenching Medium |
|---|---|---|---|---|---|---|---|---|---|
| | | C | Mn | S | P | Si | Ni | | |
| A | Commercial carbon steel | 0.49 | 0.53 | 0.036 | 0.063 | 0.10 | 0.12 | 1500 | Water |
| B | Commercial carbon steel | 0.94 | 0.33 | 0.015 | 0.009 | 0.13 | nil | 1500 | Water |
| C | Commercial carbon steel | 1.02 | 0.35 | 0.007 | 0.018 | 0.19 | trace | 1575 | Oil* |
| D | Commercial carbon steel | 1.26 | 0.34 | 0.023 | 0.024 | 0.17 | 0.16 | 1800 | Oil* |
| 4 | Iron carbon alloy | 0.63 | nil | 0.006 | 0.003 | 0.004 | nil | 1500 | Water |
| 23 | Iron carbon alloy | 0.79 | nil | 0.004 | 0.003 | 0.01 | trace | 1500 | Water |
| 9 | Iron-carbon alloy | 0.95 | nil | 0.006 | 0.003 | 0.004 | nil | 1500 | Water |

*High speed quenching oil.

*Heat Treatments* — Since the principal object of this work was to investigate the effect of carbon, it was essential to austenitize the steel completely prior to quenching. With this precaution, the diffusionless transformation product, martensite, as well as the retained austenite, could be considered to possess the same carbon content as that reported for the steel as a whole. Therefore, throughout this study, the hardening temperatures were chosen high enough so that all the cementite and ferrite were dissolved in the austenite. This, of course, is not normal practice in the heat treatment of hypereutectoid steels.

In all cases the quenching was rapid enough to suppress the separation of pearlite, bainite or proeutectiod constituents. While water quenching accomplished this purpose satisfactorily, it sometimes caused cracking in the very high carbon steels, particularly when the tempering treatments were not started immediately. Quenching in ordinary oil to avoid this cracking was not fast enough to suppress pearlite formation completely, but use of a high speed quenching oil was found to achieve a very effective compromise. Therefore, this special oil was employed for the

steels C and D, which exhibited a tendency toward cracking in a water quench.

For all except the 1.26 per cent carbon steel (Steel D), the austenitizing was conducted in a lead bath, the temperature control being approximately ± 2 degrees Fahr. (1 degree Cent.). Steel D, austenitized at 1800 degrees Fahr. (980 degrees Cent.), was heated in a carbonaceous muffle with control of ± 5 degrees Fahr. (3 degrees Cent.). Tempering temperatures were invariably held to better than ± 5 degrees Fahr. (3 degrees Cent.). Where precise timing was necessary, molten salt baths served as the tempering media; otherwise, air furnaces were used.

*X-ray Technique* — All the X-ray diffraction pictures were taken on a medium-angle focussing camera, with chromium radiation from a gas-type tube. Fine platinum powder was sprinkled on the surface of the specimens to provide reference diffraction lines on which accurate parameter measurements could be based. The surface preparation of the specimen itself was found to be quite critical, and hence, the same technique reported by Gardner, Cohen and Antia (3) was adopted here. The parameters of austenite and martensite were generally determinable to ±0.001 A.U., except where the lines became unduly broad.

*Magnetic and Dilation Measurements* — Simultaneous magnetic and dilation measurements were carried out during tempering in an apparatus constructed especially for such tempering experiments (4). The intensity of magnetization was determined with a relative precision of ± 0.2 per cent, while the dilation measurements were accurate to ± 5 millionths of an inch per inch.

*Hardness* — Rockwell C hardness measurements were made according to standard technique, and were probably accurate to ± 0.3 of a point. Throughout the course of this work, five hardness readings were taken on each of at least two specimens for each point on the hardness-tempering curves. Thus, every plotted point represents the average of ten or more hardness determinations.

*Specific Volume* — The specific volumes were measured by the weigh-in-water, weigh-in-air method. The procedure used (5) was capable of an accuracy of ±0.00002 cubic centimeters per gram.

## Retained Austenite

It has long been known that quenched carbon steels contain appreciable quantities of retained austenite, which may subse-

quently decompose during tempering under certain conditions. In order to analyze properly the martensite and retained austenite transformations which take place on tempering, it is important to establish accurately the amount of each phase present. Much work has been done in an attempt to determine quantitatively the retained austenite content as a function of the steel composition and of the quenching conditions (6). However, since there have been marked discrepancies among the reported data, it was deemed necessary to establish these values independently for the particular steels investigated here.

*Experimental* — The method employed for the retained austenite determinations was very simple, yet was found to be quite effective. Two conditions had to be fulfilled for this method to be valid: (a) Only two phases must be present in the quenched steel, and (b) these two phases must be solid solutions of known crystal structure and composition. In the present case, the first requirement was met by heat treating the steels so that no pearlite, bainite or proeutectoid constituents were formed, thus leaving only martensite and retained austenite. The second requisite was automatically satisfied by the facts that the structures of austenite and martensite are well-known (7, 8) and that the compositions of both phases are identical with that of the austenite before the quenching. Under the austenitizing conditions used, this composition may be taken without appreciable error to be that of the steel as a whole.

Once the above requirements were fulfilled, the specific volumes of the participating phases were calculated from the composition and the lattice parameters, the latter having been accurately established by X-ray work. The formula used for these calculations was

$$\bar{v} = \frac{V}{KnW}$$

where $\bar{v}$ is the calculated specific volume, V the volume of the unit cell in cubic A.U., n the number of atoms per unit cell, W the average atomic weight (corrected for dissolved manganese, silicon, carbon,[3] etc.), and K a numerical constant (related to the reciprocal of Avogadro's number), given by Jette and Foote (9) to be 1.65023.

The overall specific volume of each specimen was then

[3]Calculations were based on carbon being dissolved interstitially, the others substitutionally.

measured immediately after quenching, and the amount of retained austenite computed by the rule of mixtures. The austenite contents by weight were calculated from the formula:

$$\text{Weight \% austenite} = \frac{\bar{v}_M - \bar{v}_S}{\bar{v}_M - \bar{v}_A} \times 100,$$

while the corresponding percentages on a volume basis may be obtained by using the densities (reciprocals of the specific volumes):

$$\text{Volume \% austenite} = \frac{d_S - d_M}{d_A - d_M} \times 100,$$

where $\bar{v}_S$, $\bar{v}_M$, and $\bar{v}_A$ are the specific volumes of the steel, martensite and austenite, and $d_S$, $d_M$ and $d_A$ are their respective densities. Actually, the volume and weight contents thus derived differ by a maximum of only 1 per cent austenite (3), which is within the experimental error. Hence, for all practical purposes, the two values may be used interchangeably.

While mathematical analysis indicates that the theoretical accuracy of this specific volume method is but $\pm 3$ per cent austenite, actual measurements have demonstrated a reproducibility to within $\pm 1$ per cent. The reason for this difference is that, in practice, it is highly unlikely that all of the possible errors operate in the same direction.

In checking the reliability of this method, a specimen of Steel D (1.26 per cent carbon), quenched in high-speed oil from 1800 degrees Fahr. (980 degrees Cent.), showed 35 per cent retained austenite by the X-ray line density technique (3), 34 per cent retained austenite by the straightforward (but tedious) point-counting technique of photomicrographic analysis (10), and 35 per cent retained austenite by the above-described specific volume method. This example of the excellent agreement among the various techniques testifies to the validity of all of them. Similar agreements were found in other cases when the methods were checked against each other.

It is evident that the specific volume method is quite simple since it involves only one measurement of specific volume, once the parameters and composition are known. However, the method can be used with safety only when the martensite is untempered and when martensite and austenite are the only phases present. A small correction may be introduced for the presence of inclusions, but it is of a minor order. Particular care should be exercised when

dealing with carbon steels containing less than 0.70 per cent carbon, because then the M-point may be sufficiently high as to result in the inadvertent tempering of the martensite during the quench.

*Results* — The retained austenite contents found in the materials for which data are reported in this paper are given in Table II. These values are in fairly good agreement with the more complete set of retained austenite determinations reported by Tamaru and Sekito (11). It is apparent that, in general, the amount of retained austenite increases with carbon content. This is undoubtedly related to the fact that the martensite point is continuously lowered with increasing carbon, thus allowing less martensite to form by the time room temperature is reached.

**Table II**
**Effect of Carbon Content on Retained Austenite**

| Material | Carbon Per Cent | Austenitizing Temperature Degrees Fahr. | Quenching Medium | Retained Austenite Per Cent |
|---|---|---|---|---|
| Steel A | 0.49 | 1500 | Water | < 2** |
| Steel B | 0.94 | 1500 | Water | 13 |
| Steel C | 1.02 | 1575 | Oil* | 21 |
| Steel D | 1.26 | 1800 | Oil* | 35 |
| Alloy 4 | 0.63 | 1500 | Water | 2 |
| Alloy 23 | 0.79 | 1500 | Water | 6 |
| Alloy 9 | 0.95 | 1500 | Water | 9 |

* High speed quenching oil.
** Estimated from X-ray diffraction data.

It is also interesting to note that for equivalent carbon contents and identical quenching conditions, the commercial steel (Steel B, 0.94 per cent carbon) retains somewhat more austenite than the high-purity iron-carbon alloy (Alloy 9, 0.95 per cent carbon).

## Tempering Experiments

Several types of experiments were used to study the effect of carbon content on the transformations during the tempering of these hardened steels:[4]

A. Continuous tempering survey runs—these involved continuous heating at a rate of 5 degrees Fahr. (3 degrees Cent.) per minute, with simultaneous measurements of both dilation and magnetization.

B. Hardness-tempering experiments—these were carried out by tempering specimens for different lengths of time at suitable tem-

[4]While, in the main, the results in this section are reported only for the series of carbon steels, similar behavior was observed for the high-purity iron-carbon alloys.

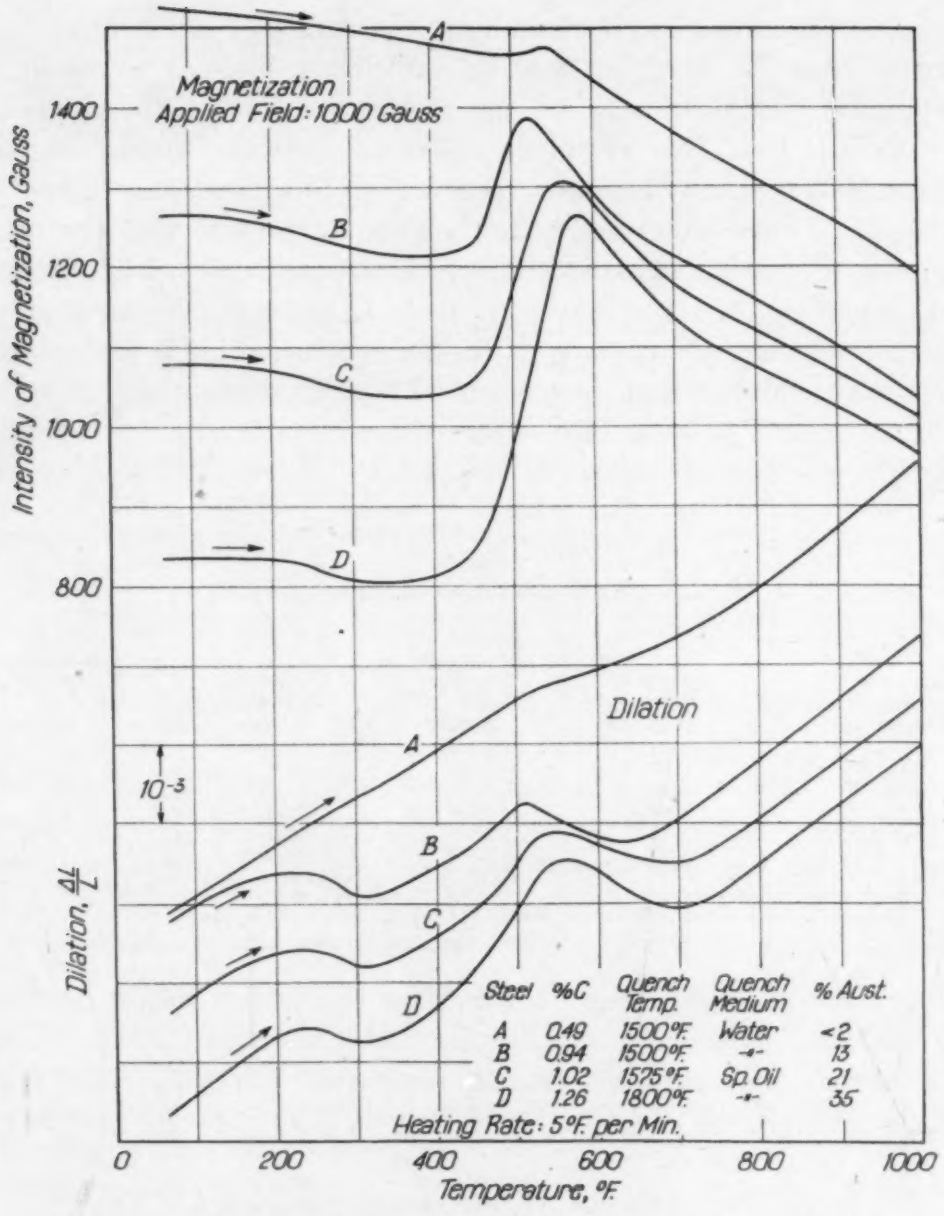


**Fig. 1—Magnetization and Dilation Curves on Continuous Heating after Quenching as Indicated. Heating Rate 5 Degrees Fahr. Per Minute.**

peratures, and then cooling to room temperature for hardness readings.

C. Isothermal tempering runs—these were made by tempering a specimen for increasing lengths of time at a given temperature, the tempering being interrupted periodically for various measurements at room temperature.

*Continuous Tempering Survey Runs*—Fig. 1 contains a set of magnetization and dilation curves obtained by heating a series of

quenched carbon steels, containing 0.49, 0.94, 1.02 and 1.26 per cent carbon, and having respectively <2, 13, 21, and 35 per cent retained austenite prior to tempering. In all of these curves, the three stages of tempering are readily discerned. However, in the 0.49 per cent carbon steel (Steel A), the effects are relatively small.

A. The First Stage. The first stage of tempering is most clearly shown in the dilation curves. This is because the decomposition of tetragonal martensite (into cubic ferrite and a transition precipitate) is more effective in causing a contraction than in influencing the magnetization. However, a slight decrease in magnetization is observed, particularly in the higher carbon steels. While it is only natural to expect the higher carbon materials to exhibit greater changes on tempering, the magnitude of these changes must be also considered with respect to the relative amount of martensite participating. For example, in Fig. 1 the contraction during the first stage appears to be rather constant for the three highest carbon steels. However, when a correction is made for the amount of martensite involved in the transformation, the contraction becomes greater the higher the carbon content. Calculations based on these data are discussed more fully in another section of this paper.

B. The Second Stage. Whereas the first stage of tempering is more readily observed in the dilation curves, the second stage is more clearly defined by the magnetic changes. This second stage reaction, the transformation of retained austenite, brings about a marked increase in magnetization as the paramagnetic austenite is converted into a ferromagnetic aggregate. Accompanying this magnetic effect is an expansion, for austenite is the densest of the constituents in steel, and therefore its decomposition produces an increase in volume.

As in the first stage reaction, Steel A (0.49 per cent carbon) undergoes very little change during the second stage. The higher carbon steels, on the other hand, display the magnetic and dilation phenomena to a greater extent, the larger the amount of austenite participating.

C. The Third Stage. The third stage of tempering involves the formation and growth of cementite (1). This cementite develops from the transition lattice which precipitates from the martensite during the first stage, and (along with ferrite) from the retained austenite during the second stage.[5] The cementite formation is accompanied by a pronounced decrease in magnetization (for cement-

[5]The evidence for this conversion is presented in reference (1).

ite is paramagnetic at these temperatures while the transition precipitate is ferromagnetic), and a well-defined contraction. At first glance, the magnitude of these changes does not seem to vary greatly with carbon content (or amount of retained austenite), except in the case of Steel A (0.49 per cent carbon) where again the effects are quite minor. However, their actual dependence on both carbon content and amount of retained austenite will be shown later.

Above a temperature of about 750 degrees Fahr. (400 degrees Cent.) the magnetization and dilation curves exhibit normal thermal coefficients, and show no signs of further structural change.

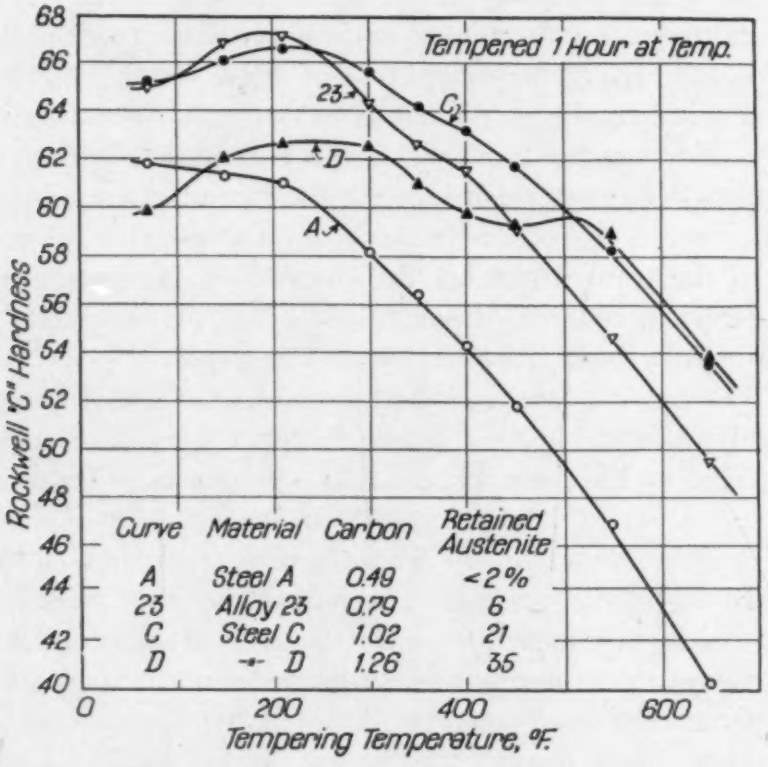


Fig. 2—Hardness-Tempering Curves, Showing Hardness after One-Hour Tempering at Various Temperatues.

*Hardness-Tempering Experiments*—In order to correlate hardness changes with the different stages of tempering shown above, a detailed hardness investigation was made at various tempering temperatures and times. For this particular study, Steel B (0.94 per cent carbon) has been replaced by Alloy 23 (0.79 per cent carbon) in the series of materials tested.

Fig. 2 presents the standard hardness-tempering curves for the four materials, the tempering time being 1 hour at temperature.

Figs. 3, 4 and 5 show the curves for Alloy 23 (0.79 per cent carbon), Steel C (1.02 per cent carbon) and Steel D (1.26 per cent carbon) respectively, and demonstrate the change in appearance of the tempering curves for increasing tempering times from 0.1 hour to 100 hours.

Several features of these curves bear further discussion:

A. With the exception of Steel A (0.49 per cent carbon), all the curves show decided increases in hardness during the first stage of tempering. This is noticeable not only with increasing tempera-

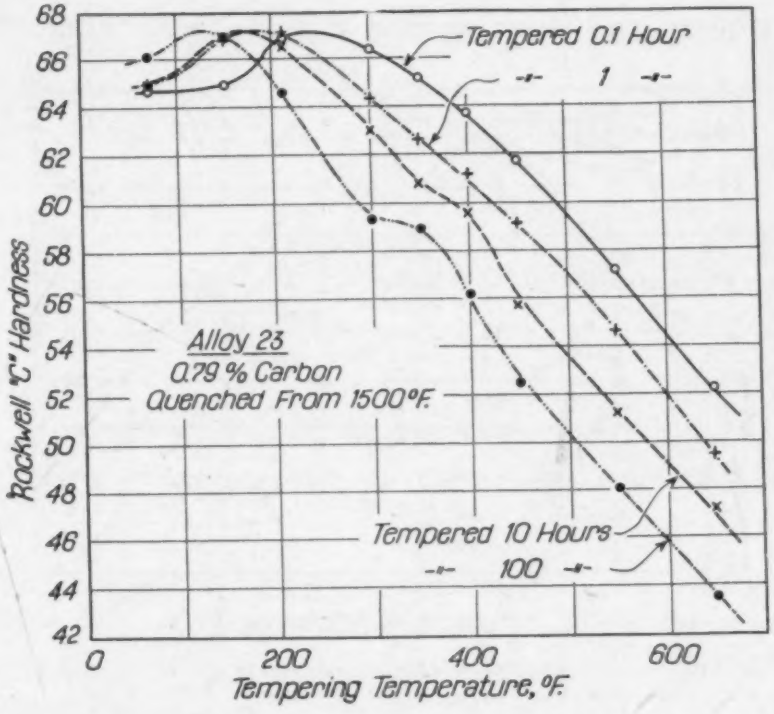


Fig. 3—Hardness-Tempering Curves for Alloy 23 (0.79 Per Cent Carbon, 6 Per Cent Retained Austenite).

ture, but with increasing time at room temperature and at 150 degrees Fahr. (65 degrees Cent.). In fact, Steel D (1.26 per cent carbon) gains 2.4 points Rockwell C on aging at room temperature for 100 hours. Even the relatively low carbon Steel A (0.49 per cent carbon) displays a pronounced tendency toward retarded softening through the first stage. This general behavior has been observed before (12-14), and is not unexpected in view of the nature of the first stage reaction. The precipitation from martensite of a transition structure is directly analogous to age-hardening precipitation in numerous non-ferrous systems (15-19).

B. There is a secondary hardening effect in all the materials, again excepting Steel A (0.49 per cent carbon). This secondary hardening, which is most readily seen in Fig. 5 for Steel D (1.26 per cent carbon), has been properly attributed to decomposition of retained austenite. Austenite is a comparatively soft constituent, while its decomposition product is appreciably harder. Nevertheless, it appears that a rather large amount of austenite is required to produce marked secondary hardening. Steel D (1.26 per cent carbon), which contains 35 per cent retained austenite prior to tempering, shows a low initial hardness ($R_c$ 58.6) due to the presence of this soft constituent, and also a distinct increase in hardness when the

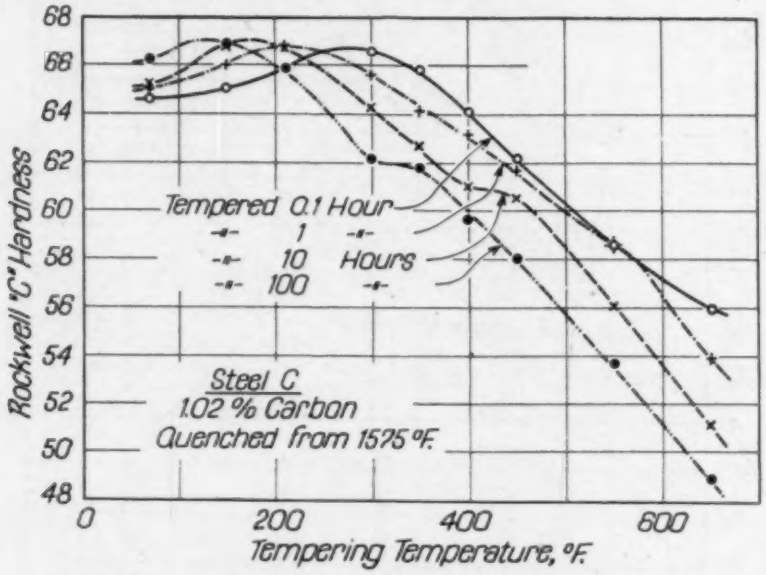


Fig. 4—Hardness-Tempering Curves for Steel C (1.02 Per Cent Carbon, 21 Per Cent Retained Austenite).

austenite decomposes during the second stage of tempering. On the other hand, Steel C (1.02 per cent carbon), containing 21 per cent retained austenite prior to tempering, has high initial hardness ($R_c$ 64.6) and reveals the secondary hardening reaction only through retarded softening. Almost identical results, both as to initial hardness and secondary hardening, are obtained with Alloy 23 (0.79 per cent carbon), which contains but 6 per cent retained austenite on quenching. Presumably the amount of retained austenite has relatively little effect on the hardness until it makes up something over one-fifth of the structure.

C. These curves, and particularly Fig. 5, illustrate nicely the time effect on tempering. In general, the longer the tempering time

the lower the temperature of peak hardness in the first stage, and the lower the temperature of the secondary hardening in the second stage. The actual maximum hardness attained during the first stage does not seem to be much affected by time.

D. The third stage of tempering (formation and growth of cementite) as well as the stress-relief between the first two stages are both softening influences, as has been discussed elsewhere by the authors (1).

*Isothermal Tempering Runs*—A more detailed picture of the individual stages of tempering may be obtained from a consideration

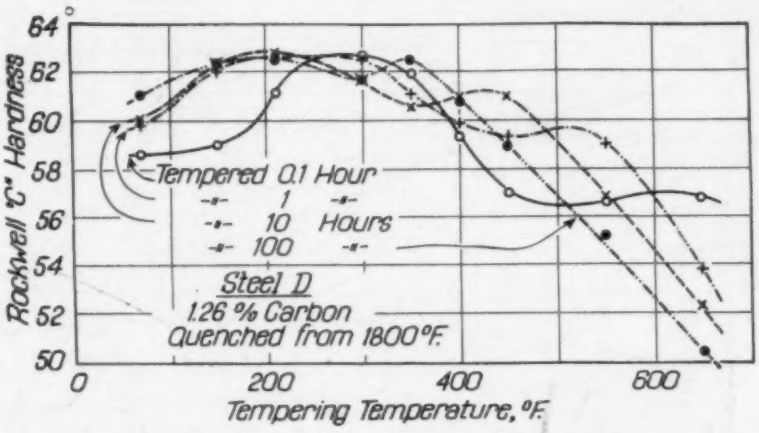


Fig. 5—Hardness-Tempering Curves for Steel D (1.26 Per Cent Carbon, 35 Per Cent Retained Austenite).

of isothermal changes. Fig. 6 shows the changes in various properties of Steels B (0.94 per cent carbon), C (1.02 per cent carbon) and D (1.26 per cent carbon) on tempering at 212 degrees Fahr. (100 degrees Cent.) up to 100 hours, thus encompassing the first stage of tempering. At this temperature, it is evident that most of the reaction is complete within 10 hours. By that time, the major amount of the contraction (specific volume change) has taken place, the hardness has reached its maximum, a slight decrease in magnetization has occurred, and the martensite tetragonality has essentially disappeared. After 10 hours, the specific volume curves tend to flatten out, the magnetization increases somewhat, and the hardness starts to decrease. These effects, particularly the increase in magnetization, are indicative of stress-relief rather than of another phase transformation.

The degree of tetragonality in the martensite is sufficiently high to permit fairly accurate parameter measurements up to about 1 hour

at 212 degrees Fahr. (100 degrees Cent.). Thereafter, however, the (110)-(101) doublet merges into a single broad line, the center of which is located at a slightly higher angle than the ferrite or martensite "a" parameter would allow. Consequently, it is assumed that some tetragonality (or a distorted cubic condition) still exists, though it is not a distinctly measurable quantity. This is represented

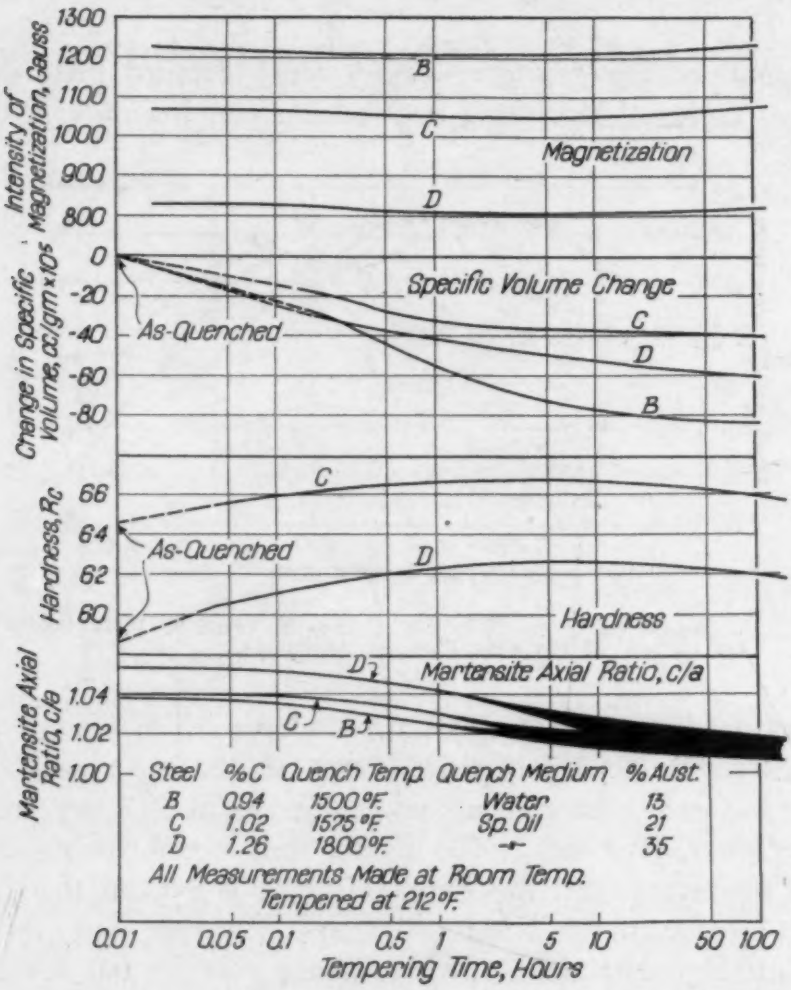


**Fig. 6—Effect of Tempering Time at 212 Degrees Fahr. (100 Degrees Cent.) on Properties of High Carbon Steels.**

in Fig. 6 by the broad band, the width of which shows the approximate uncertainty of the parameter determinations.

There appears to be no effect of carbon content upon the *rate* of this first stage reaction. However, the *amount* of contraction is seen to vary somewhat irregularly with respect to the carbon content. This behavior, of course, is caused by the presence of vary-

ing amounts of retained austenite (thus, of martensite), the effect of which has not been compensated for in the as-measured specific volume curves. It is also observed that the higher carbon content of Steel D (1.26 per cent carbon) results in a 4-point Rockwell C increase in hardness, while Steel C (1.02 per cent carbon) exhibits a hardening of but 2 points Rockwell C.

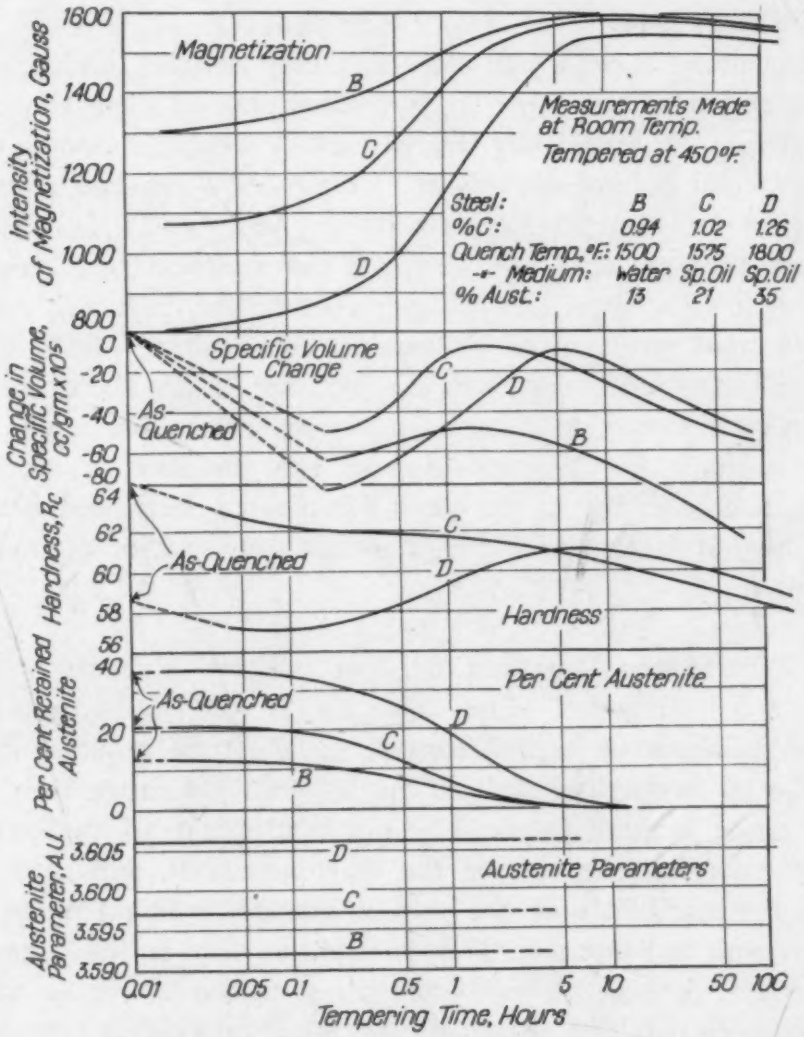


**Fig. 7—Effect of Tempering Time at 450 Degrees Fahr. (230 Degrees Cent.) on Properties of High Carbon Steels.**

Fig. 7, which represents isothermal tempering at 450 degrees Fahr. (230 degrees Cent.), depicts the second stage of tempering, and the beginning of the third stage. The decomposition of retained austenite is shown by the large magnetization increase, the accompanying expansion, and the secondary hardening effects. The

succeeding slight decrease in magnetization after about 10 hours' tempering, the large decrease in specific volume, and the beginning of softening are indicative of the progressive entrée of the third stage. According to Fig. 7, the decomposition of retained austenite[6] is completed in about 5 hours at 450 degrees Fahr. (230 degrees Cent.) in Steels B (0.94 per cent carbon) and C (1.02 per cent carbon), while about 10 hours is required for its complete decomposition in Steel D (1.26 per cent carbon).

After only 3 or 4 per cent austenite remains undecomposed, the contraction of the third stage (which sets in some time before the austenite is completely transformed) becomes more evident and the specific volume diminishes. This point is reached after about 2 hours at 450 degrees Fahr. (230 degrees Cent.) for Steels B (0.94 per cent carbon) and C (1.02 per cent carbon), and after about 5 hours for Steel D (1.26 per cent carbon). It also coincides with the most pronounced "secondary hardening" effect. Thereafter, the formation and growth of cementite brings about softening, as well as a decrease in volume and in magnetization.

Throughout the decomposition of the austenite, its parameter does not change in any of the steels examined. This implies that its transformation is carried through without any major alteration of composition.

## Critical Analysis of Volumetric Effects

The influence of carbon content on the time required for the first stage of tempering, and on the temperature range over which it takes place, is quite small. The principal action of carbon seems to lie in enlarging the size of the martensite cell, and thus in increasing the magnitude of the volume changes brought about when the martensite decomposes. This is true not only in the commercial carbon steels, but in the high-purity iron-carbon alloys as well. In an attempt to analyze these effects quantitatively, a number of measurements were made, based on heating-dilation curves such as those shown in Fig. 1. By projecting the normal temperature coefficient curve back from 350 degrees Fahr. (175 degrees Cent.) (where the first stage of tempering is essentially complete on

[6]The retained austenite contents plotted in Fig. 7 were obtained with the aid of magnetic measurements which accurately yielded the fractional variations in the amount of austenite during tempering. When these determinations were coupled with the austenite contents initially present (cf. Table II), it was possible to calculate the absolute amount of austenite remaining after the various tempering treatments.

**Table III**
**General Volumetric Data**

| Column | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Measured Volume Changes | | | Calculated Specific Volumes | | |
| Material | Carbon Per Cent | Austenitizing Temperature Degrees Fahr. | Quench Medium | Retained Austenite Per Cent | All 3 Stages $\Delta V/Vs$ | 1st Stage $\Delta V/Vs$ | 2nd & 3rd Stages $\Delta V/Vs$ | Martensite cc/gm | Austenite cc/gm | Ferrite & Cementite cc/gm |
| Steel A | 0.49 | 1500 | Water | <2 | −0.0044 | −0.0012 | −0.0032 | 0.12868 | 0.12320 | 0.12742 |
| Steel B | 0.94 | 1500 | Water | 13 | −0.0116 | −0.0045 | −0.0071 | 0.12984 | 0.12471 | 0.12766 |
| Steel C | 1.02 | 1575 | Sp. Oil | 21 | −0.0099 | −0.0041 | −0.0058 | 0.13014 | 0.12518 | 0.12780 |
| Steel D | 1.26 | 1800 | Sp. Oil | 35 | −0.0079 | −0.0042 | −0.0037 | 0.13074 | 0.12579 | 0.12788 |
| Alloy 4 | 0.63 | 1500 | Water | 2 | −0.0083 | −0.0028 | −0.0055 | 0.12891 | 0.12347 | 0.12736 |
| Alloy 9 | 0.95 | 1500 | Water | 9 | −0.0117 | −0.0047 | −0.0070 | 0.12970 | 0.12453 | 0.12748 |

heating) to room temperature, the amount of contraction encountered in the first stage of tempering was ascertained. In the same way, the total contraction for all three stages of tempering was measured by considering the cooling curve after heating to 1000 degrees Fahr. (540 degrees Cent.). To aid in general calculations the unit length changes thus obtained, $\frac{\Delta L}{L}$, were converted into unit volume changes, $\frac{\Delta V}{V}$, by multiplying by three.[7] The resulting values are given in columns 5 and 6 of Table III. Column 7, presenting the unit volume change for the combined second and third stages of tempering, is obtained by subtracting the effect of the first stage (column 6) from the total over-all contraction (column 5). Columns 8, 9 and 10 of Table III contain the specific volumes of the three well-defined structures, martensite, austenite and ferrite plus cementite, calculated from the known lattice parameters, crystal structure and composition. The values computed for the ferrite plus cementite mixture agree very closely with the experimentally

**Table IV**
**First Stage Calculations**

| Column | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| | | Structural Composition | | Volume Change Per Unit of Martensite | | | |
| Material | Carbon Per Cent | Austenite Per Cent | Martensite Per Cent | First Stage $\Delta V/V_S$ | First Stage $\Delta V/V_M$ | Complete Martensite Decomposition $\Delta V/V_M$ | Column 5 / Column 6 |
| Steel A | 0.49 | <2 | >98 | −0.0012 | −0.0012 | −0.0098 | 0.12 |
| Steel B | 0.94 | 13 | 87 | −0.0045 | −0.0052 | −0.0168 | 0.31 |
| Steel C | 1.02 | 21 | 79 | −0.0041 | −0.0052 | −0.0180 | 0.29 |
| Steel D | 1.26 | 35 | 65 | −0.0042 | −0.0064 | −0.0219 | 0.29 |
| Alloy 4 | 0.63 | 2 | 98 | −0.0028 | −0.0029 | −0.0120 | 0.24 |
| Alloy 9 | 0.95 | 9 | 91 | −0.0047 | −0.0052 | −0.0171 | 0.30 |

measured specific volumes after tempering at 1000 degrees Fahr. (540 degrees Cent.).

*A. First Stage Calculations*—Based on the data presented in Table III, further calculations were made relating to the first stage of tempering. The results of these calculations are given in Table IV. In this table, column 4 is identical with column 6 of Table III, and is the observed volume change (referred to room temperature) encountered during the first stage of tempering.

[7] In the following discussion, $V_S$, $V_M$ and $V_A$ are the volumes of the steel, martensite and austenite respectively.

Column 5 is the volume change corrected for the amount of martensite participating. In other words, retained austenite does not contribute to the first stage, and should not be included in the actual contraction figure. This column 5 is, then, the actual volume change per *unit* of *martensite*. Column 6, giving $\frac{\Delta V}{V_M}$ for complete martensite decomposition to ferrite and cementite, was computed from the specific volume data in Table III.

An inspection of Table IV reveals that, in general, the higher the carbon content of martensite, the greater is its contraction in the first stage of tempering, providing the measured contraction of the specimen is corrected for the non-participating retained austenite (cf. column 5). Further information may be gained from these data if the amount of martensite contraction encountered in the first stage is compared to the volume change expected when martensite decomposes completely to ferrite and cementite (column 5 vs. column 6). The fraction of the total martensite decomposition occurring in the first stage is given in column 7.

Except for Steel A (0.49 per cent carbon) and Alloy 4 (0.63 per cent carbon), this fraction is found to be about 0.3, and does not appear to vary with carbon content.[8] Such a constant value for the fractional decomposition leads to important implications. It has been postulated that the tempering of martensite in the first stage results in a precipitation of cementite (25), or cementite molecules (14). While the latter case is very unlikely for reasons which are fully discussed elsewhere (1), the former idea—precipitation of cementite—is a distinct possibility. However, the present calculations show that it, too, is not the correct reaction. The data in Table IV predict that a new transition phase comes into existence on martensite decomposition, with a volume decrease only about three-tenths that required for the complete decomposition of martensite into ferrite and cementite. That the actual measured contraction increases with carbon content, while the *fractional* change remains constant, is further support of such a phenomenon.

One may be tempted, in defense of the cementite-precipitation theory, to explain away the three-tenths ratio by saying that only

[8]The divergent values, 0.24 for Alloy 4 and 0.12 for Steel A, are undoubtedly caused by premature martensite tempering during the quench, since the M-points for these lower carbon materials are 600 degrees Fahr. (315 degrees Cent.) and 700 degrees Fahr. (370 degrees Cent.) respectively (21). It appears, therefore, that when the carbon contents are relatively low, part of the first stage of tempering occurs during the hardening operation.

30 per cent of the cementite precipitates early in the tempering process. However, there is no reason to believe that this transformation would be divided into two so distinct steps, separated by a few hundred degrees of temperature. X-ray diffraction work likewise refutes this possibility. The loss in tetragonality, shown in Fig. 6, which follows very closely the removal of carbon, is much greater than would correspond to 30 per cent of cementite precipitation. In addition to these calculations, other experiments have shown that on cooling a piece of plain carbon steel which

**Table V**
**Specific Volume of Tempered Martensite**

| Column | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| | | Structural Composition | | | |
| Material | Carbon Per Cent | Austenite Per Cent | Martensite Per Cent | Volume Change Martensite to Tempered Martensite $\Delta V/V_M$ | Specific Volume of Tempered Martensite cc/gm |
| Steel A | 0.49 | <2 | >98 | −0.0012 | 0.12853* |
| Steel B | 0.94 | 13 | 87 | −0.0052 | 0.12916 |
| Steel C | 1.02 | 21 | 79 | −0.0052 | 0.12947 |
| Steel D | 1.26 | 35 | 65 | −0.0064 | 0.12990 |
| Alloy 4 | 0.63 | 2 | 98 | −0.0030 | 0.12854* |
| Alloy 9 | 0.95 | 9 | 91 | −0.0052 | 0.12903 |

*These values are undoubtedly high, because of the partial tempering of martensite during quenching (high M-point).

has been tempered well into the second stage, no cementite Curie point can be detected (1). This may be taken as additional evidence of the non-existence of cementite prior to the third stage of tempering. Transition structures, such as are indicated here for the precipitate from martensite during low-temperature tempering, and as part of the transformation product of retained austenite, have been reported before in precipitation hardening studies (16-19). Indeed, there is already some X-ray evidence to confirm the existence of a transition lattice in tempered martensite (20).

*B. Specific Volume of Tempered Martensite* — Knowing the amount of contraction experienced in the transformation from tetragonal martensite to tempered martensite as well as the specific volume of the tetragonal martensite, it becomes relatively simple to calculate the specific volume of the tempered martensite. This has been done for the materials under investigation, and the results are tabulated in Table V. It will be noted that the specific volume of tempered martensite increases with increasing carbon content, and lies between the values for martensite and for ferrite plus

cementite, as would be expected from the results reported in Table IV. The values given for Steel A (0.49 per cent carbon) and Alloy 4 (0.63 per cent carbon) may be somewhat high, for the volume changes in the first stage are less than expected because of inadvertent tempering during quenching.

*C. Separation of Second and Third Stages* — It has been postulated (1) that the retained austenite decomposition product, while very similar to bainite in appearance at high magnifications, has undoubtedly the same state of aggregation as the tempered martensite. That is, it too is composed of cubic ferrite and a transition precipitate. X-ray diffraction results indicate that this aggregate is identical in constitution with tempered martensite, for no change in the pattern (except for the disappearance of the

**Table VI**
**The Second and Third Stages of Tempering**

| Column | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| | | | | Calculated Volume Changes | | |
| | | Structural Composition | | Per Unit of Austenite | Second Stage Per Unit of Steel | Third Stage |
| | Carbon | Austenite | Martensite | Austenite to Decomposition | Austenite to Decomposition | Formation of |
| Material | Per Cent | Per Cent | Per Cent | Product $\Delta V/V_A$ | Product $\Delta V/V_S$ | Cementite $\Delta V/V_S$ |
| Steel A | 0.49 | <2 | >98 | +0.0432 | +0.0009 | -0.0087* |
| Steel B | 0.94 | 13 | 87 | +0.0358 | +0.0047 | -0.0116 |
| Steel C | 1.02 | 21 | 79 | +0.0342 | +0.0072 | -0.0129 |
| Steel D | 1.26 | 35 | 65 | +0.0322 | +0.0113 | -0.0155 |
| Alloy 4 | 0.63 | 2 | 98 | +0.0411 | +0.0008 | -0.0092* |
| Alloy 9 | 0.95 | 9 | 91 | +0.0362 | +0.0033 | -0.0120 |

*These values are undoubtedly high. See footnote on page 351.

austenite lines) is brought about by the austenite decomposition; the tempered martensite lines are merely enforced.

Inasmuch as the specific volume of tempered martensite is now known, and since the austenite decomposition product may be taken to possess the same specific volume as the tempered martensite, it becomes possible to isolate the volumetric effects of the overlapping second and third stages of tempering. Results of calculations based on these figures are given in Table VI. In this table, column 4 lists the expansions per unit volume of austenite, while column 5 shows the unit volume changes for the steel as a whole, containing the indicated amounts of austenite. This is the expansion due to the *second stage of tempering,* unobscured by the third stage. Similarly, column 6 gives the contractions during the *third stage*

*of tempering,* i.e., due to the ultimate formation of a cementite-ferrite aggregate from the tempered martensite of the first stage and from the austenite decomposition product of the second stage. These values were computed from the specific volume data in column 10, Table III, and column 5, Table V.

Among the interesting features of these calculations is the fact that the higher the carbon content, the less is the unit expansion caused by austenite decomposition (column 4). This arises from the fact that the specific volume of austenite increases more rapidly with carbon than does that of the decomposition product. In spite of this decreased unit volume change with increasing carbon, the actual expansion experienced *increases* with carbon (column 5).

**Table VII**
**Relationship Between Calculated and Observed Volume Changes**

| Column | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| | | Structural Composition | | Volume Change Combined Second and Third Stages | | |
| Material | Carbon Per Cent | Austenite Per Cent | Martensite Per Cent | Calculated $\Delta V/V_S$ | Observed $\Delta V/V_S$ | Ratio: Observed / Calculated |
| Steel A | 0.49 | <2 | >98 | −0.0078 | −0.0032 | 0.4* |
| Steel B | 0.94 | 13 | 87 | −0.0069 | −0.0071 | 1.0 |
| Steel C | 1.02 | 21 | 79 | −0.0057 | −0.0058 | 1.0 |
| Steel D | 1.26 | 35 | 65 | −0.0042 | −0.0037 | 0.9 |
| Alloy 4 | 0.63 | 2 | 98 | −0.0084 | −0.0055 | 0.7* |
| Alloy 9 | 0.95 | 9 | 91 | −0.0087 | −0.0070 | 0.8 |

*These values are low for reasons stated in the footnote on page 351.

This, of course, is because the progressively increasing amounts of retained austenite more than compensate for the lessened volume change per unit austenite. The third stage contraction also becomes more pronounced with increasing carbon content, as observed in column 6.

It should be pointed out that these calculations pertaining to the second and third stages cannot be confirmed directly by experiment because of their overlapping nature. However, a check as to their over-all validity may be provided by comparing the calculated combined second and third stage volume changes with those observed experimentally. This has been done in Table VII. Columns 5 and 6 of Table VI have been added together to make up column 4 of Table VII, the *calculated* combined second and third stage volume change. Column 5 of Table VII is the *observed* combined second and third stage volume change, and is taken from column

7 of Table III. Comparison of these two sets of data, whose ratio is given in column 6 of Table VII, shows that excellent agreement is obtained between the calculated and the observed effects, and lends considerable weight to the data herein presented. Steel A (0.49 per cent carbon) and Alloy 4 (0.63 per cent carbon) are out of line, but the reasons for these deviations have been given earlier (cf. footnote number 8).

## Conclusions

1. The retained austenite content of plain carbon steel and iron-carbon alloys consisting of an untempered martensite-austenite aggregate can be calculated from a knowledge of the parameters, composition and specific volume of the steel.
2. The amount of retained austenite increases rapidly with the carbon content dissolved during the austenitizing treatment.
3. High-purity iron-carbon alloys retain somewhat less austenite on quenching than commercial steels of the same carbon content, but the mechanism of tempering is the same.
4. The three stages of tempering are observed in all the materials investigated (0.49 to 1.26 per cent carbon).
5. Carbon has a negligible influence on the rate of martensite decomposition during the first stage. However, increasing carbon intensifies the property changes if allowance is made for the amount of martensite involved. The specific volume of the tempered martensite has been calculated in each case.
6. Precipitation of cementite during the first stage is not indicated, for only three-tenths of the required contraction is observed.
7. The magnetic and volumetric effects accompanying the second stage are dependent on both the carbon content and the quantity of retained austenite. The rate of reaction is only slightly influenced by the carbon content.
8. Secondary hardening due to austenite decomposition on tempering becomes quite pronounced when more than 20 per cent austenite is retained on quenching.
9. The third stage of tempering is a softening reaction. The various property changes during this stage are a direct function of the carbon content.
10. The volumetric effects of the second and third stages, which normally overlap, may be separated by suitable calculations. The data thus derived agree with the over-all observed changes.

ACKNOWLEDGMENTS

The authors wish to acknowledge the kind assistance of A. W. Schneble, Jr., T. B. Winkler, and Dara P. Antia in various phases of this work.

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## DISCUSSION

**Written Discussion:** By Otto Zmeskal, research metallurgist, Universal-Cyclops Steel Corp., Bridgeville, Pa.

It has been a pleasure to read this paper, which confirms the advantages of the instrument developed at Massachusetts Institute of Technology Metallurgical Laboratories, that permits simultaneous measurement of magnetization and length changes.

The papers of Dr. Cohen and his associates have revealed a variety of methods for determining the retained austenite contents of steels. The method presented by Dr. Fletcher and Dr. Cohen is, perhaps, the most accurate. How do the authors reconcile the hardening at temperatures of boiling water of low alloy martensite with the softening of high alloy martensite? Would it be plausible to state that the precipitate in plain carbon steels[9] is $Fe_xC$, where x is greater than 3, and that in high speed steels the first precipitate is $Fe_3C$? In the papers of Dr. Cohen all references to the experimental details on specific volume measurements are made to the paper of Cohen and Koh.[10] The descriptions of the precautions necessary to obtain the high accuracy reported of plus or minus 0.00002 cc per gram are not given. The writer feels that it would be very desirable to have the details of the procedure followed by Dr. Fletcher and Dr. Cohen available in the TRANSACTIONS.

**Written Discussion:** By Robert S. Rose, sales metallurgist, Vanadium-Alloys Steel Co., Boston, Mass.

This paper impresses me as an important contribution to the technical literature on plain carbon steel. The excellent agreement between the three techniques for the determination of retained austenite indicates the reliability of all three, even though the prerequisite of two solid solutions limits the applicability of the calculation (lattice parameter, etc.) method. Nevertheless, it has been ingeniously employed in this particular research.

Fig. 6 appears to offer additional evidence that the high hardness of martensite cannot be fully explained by lattice distortion. Indeed, the hardness is at a maximum when the martensite axial ratio approaches unity.

[9]G. Kurdjumow, *Metallurg,* 1940, p. 96-125.

[10]M. Cohen and P. K. Koh, "The Tempering of High Speed Steel," TRANSACTIONS, American Society for Metals, Vol. 27, 1939, p. 1015-1051.

The evidence that a structure other than cementite is precipitated during the first stage seems conclusive, but it would be of interest to have the authors elaborate a bit as to the probable constitution of this structure. The implication seems to be that as initially precipitated it is not a specific or stable compound, but rather undergoes continuous size and chemical change to cementite as the end product.

The effect of carbon content on the quantity of retained austenite is, in some respects, surprising. First, previous estimates of retained austenite in quenched 0.90 per cent carbon steel, after appropriate heating to dissolve all carbides, have been in the vicinity of 15 to 20 per cent. Second, the differences between the quantity of austenite, for the 0.49 per cent carbon and the 0.94 per cent carbon is 11 per cent, and the 0.94 per cent carbon and 1.02 per cent carbon is 8 per cent, are somewhat inconsistent with the slope of the Ar" as a function of carbon content.[11, 12] The graphs show a linear relationship up to about 0.90 carbon and a decrease in slope thereafter. Based upon the austenite contents shown by the authors, the Ar", which must be the controlling factor, would be delineated with a fairly flat slope up to 0.94 per cent carbon and decided increase in slope with higher carbon contents.

The soaking time and details of the metallographic technique used to assure the absence of undissolved carbide are not reported in this paper, but it is obvious that even traces of incomplete solution would upset the Ar" to austenite relationship. The inhomogeneity of austenite has been shown to have a pronounced effect on hardenability[13] and special etches[14, 15] have been suggested to determine the presence of carbide and gradients in carbon concentration. It is possible, therefore, that the apparent anomalies in retained austenite content may be traceable to a lack of homogeneity in the austenite at heat. It is also of some significance to inquire as to the effect of the change in quenching media between the two lower and two higher carbon steels, particularly since one of the authors in a previous publication[16] did in fact show that a difference in retained austenite resulted from variations in the drasticity of the quench.

### Authors' Reply

A significant point has been raised by Dr. Zmeskal with regard to the increase in hardness observed in these high carbon steels during the first stage of tempering, while no analogous increase is found in the highly alloyed high speed steels. This apparent anomaly is, of course, due to the fact that the first-stage hardening depends primarily not upon the alloy content, but upon the carbon content dissolved in the martensite. Carbon undoubtedly plays a much more important role in the decomposition of tetragonal martensite and formation of a transition precipitate than do any of the common alloying

[11]A. B. Greninger and A. R. Troiano, "Kinetics of the Austenite-Martensite Transformation in Steel," TRANSACTIONS, American Society for Metals, Vol. 28, 1940, Fig. 15, p. 558.

[12]L. H. Chiswik, Personal Communication.

[13]Roberts and Mehl "Effect of Inhomogeneity in Austenite on Rate of the Austenite-Pearlite Reaction in Plain Carbon Steel," T. P. 1568, American Institute of Mining and Metallurgical Engineers.

[14]E. Walldow, "The Mechanism of the Solution of Cementite in Carbon Steel and Influence of Hetrogeneity"

[15]M. Baeyertz, "The Use of Chromic Acid in Electrolytic Etching of Iron and Steel."

[16]O. Zmeskal and M. Cohen, "The Tempering of Two High Carbon-High Chromium Steels," TRANSACTIONS, American Society for Metals, Vol. 31, 1943, p. 380.

elements. Therefore, in a low alloy high carbon steel, a substantial increase in hardness is observed when tetragonal martensite decomposes, while in a high alloy steel with considerably less carbon in the martensite (such as in high speed steel) the first stage may easily result in some softening. On the other hand, in steels with martensite containing both high carbon and high alloy (such as the high carbon, high chromium steels) the first stage of tempering again results in hardening.

Dr. Zmeskal has also asked us for a more complete description of our method of measuring specific volumes to an accuracy of 0.00002 cubic centimeter per gram. Briefly, it consists in weighing the specimen in air, then in water, and computing the specific volume by means of the formula

$$\bar{v} = \frac{W_a - W_w}{d_w \, W_a}.$$

$W_a$ and $W_w$ are the weights of the specimen in air and in water respectively, while $d_w$ is the density of water at the temperature used. Values of $d_w$ may be obtained from any chemical handbook. To secure the required precision, the technique of weighing in water must be carefully worked out and a standardized practice adopted. Following is the procedure which has been in use at M.I.T.

Christian Becker "Chainomatic" analytical balances were used for the weighings, the sensitivity being at least 0.00005 gram at the loads used in this work.

The specimen may be any shape or size, but the most convenient weight for our purposes has been about 20 grams. The sharp edges and corners on the specimen are rounded, and all surfaces polished with No. 1 emery paper. The specimen is degreased and cleaned by washing (without intermediate drying) in benzene, ether and alcohol successively, and then dried with the moderate blast of air from an ordinary hair dryer. This process is repeated immediately before making a weighing in water. Needless to say, the specimen is never handled with the fingers after cleaning.

The actual wet-weighing is done by immersing the specimen in a 250-cubic centimeter beaker about two-thirds full of water, supported by a small wooden or metal bridge which straddles the balance pan. The specimen is held in a frame made of bent copper wire (0.05 inch diameter), the shape of which is unimportant as long as it supports the specimen. This frame, in turn, is suspended by a fine platinum wire (0.006 inch diameter) which hooks on to the balance arm. The entire frame and specimen are under water during the weighing, so the only surface tension effect is on the platinum wire. This is the reason for reducing the size of the wire to the finest possible. In order further to reduce this surface tension effect, and to facilitate "wetting" of the specimen and frame without an adherent air film, a small quantity of wetting agent is used in the water. A 0.004 per cent addition of "Sorbitol Derivative (Lauric)", made by the Atlas Powder Company, has been found to increase markedly the sensitivity of the wet-weighing.

In carrying out a determination, the specimen and frame should have no adherent air bubbles; rapid alternate immersion usually dispels any that may be persistent. The correct weight is always approached from the *high* side,

rather than from the *low* side as is ordinary practice. This is to prevent inordinate wetting of the platinum wire, which results in greatly decreased sensitivity and accuracy in weighing. This also means that the "method of swings" cannot be effectively used; the pointer is not allowed to pass the zero point to the right.

The frame is then weighed in water alone, so that its weight may be deducted to obtain the weight of the specimen alone in water. It has been found that the effect of the difference in water-level if the specimen is not present is insufficient to justify any correction (i.e., for a specimen of about 20 grams, and a 250-cubic centimeter beaker with 0.006-inch diameter platinum suspension wire). The temperature of the water is measured after each weighing to the nearest tenth of a degree Cent.

A summary of the steps follows:

(1) Prepare and clean specimen. Round edges and corners, polish with No. 1 emery, clean in benzene, ether and alcohol, and dry.
(2) Weigh specimen in air ($W_a$).
(3) Weigh specimen and frame in water ($W_w + W_f$).
(4) Weigh frame alone in water ($W_f$).
(5) Measure water temperature (to determine $d_w$).
(6) Substitute in formula

$$\bar{v} = \frac{W_a - [(W_w + W_f) - W_f]}{d_w W_a}.$$

If $W_a$, $W_w + W_f$, and $W_f$ are each measured to the nearest tenth of a milligram, and the temperature to the nearest tenth of a degree Cent., the accuracy in $\bar{v}$ is $\pm$ 0.000016 cubic centimeter per gram.

It is apparent that an increase in either the mass of the specimen or the density of the wet-weighing medium or both should permit added precision in these specific volume measurements. More accurate methods designed to take advantage of these factors are now under study. It should be emphasized, however, that higher-precision determinations can only be effectively utilized in following the specific volume changes of a *given* specimen as a function of treatment. Ordinarily, higher precision is not justified when comparisons of various specimens are involved, since even adjacent samples of annealed steel may then show disturbing differences.

Mr. Rose's discussion brings up several interesting matters. The authors do not wish to theorize here on the entertaining question of martensite hardness. However, they cannot agree that the experiments reported in this paper on tempering cast any shadow on the lattice distortion explanation of martensite hardness. The fact that tempered martensite (in which the axial ratio is practically unity) is harder than quenched martensite in high carbon steel could simply mean that the precipitated transition phase is more efficacious in obstructing plastic deformation than the lattice distortion inherent in the tetragonal martensite.

As Mr. Rose observes, the transition precipitate is not a definite nor stable compound. On the other hand, its conversion into cementite is not rapid nor continuous. The transition precipitate seems to form with surprising ease on heating, but then it persists for a few hundred degrees before it decomposes

into the more stable cementite. Our picture of this process is given on page 30 of reference 1.

It is risky to assume that the dependence of retained austenite content on the dissolved carbon can be predicted from the relationship between the M-point (or Ar") and the carbon content. During the hardening quench, the amount of austenite left in the steel when room temperature is reached depends not so much on the temperature at which the austenite-martensite transformation starts,

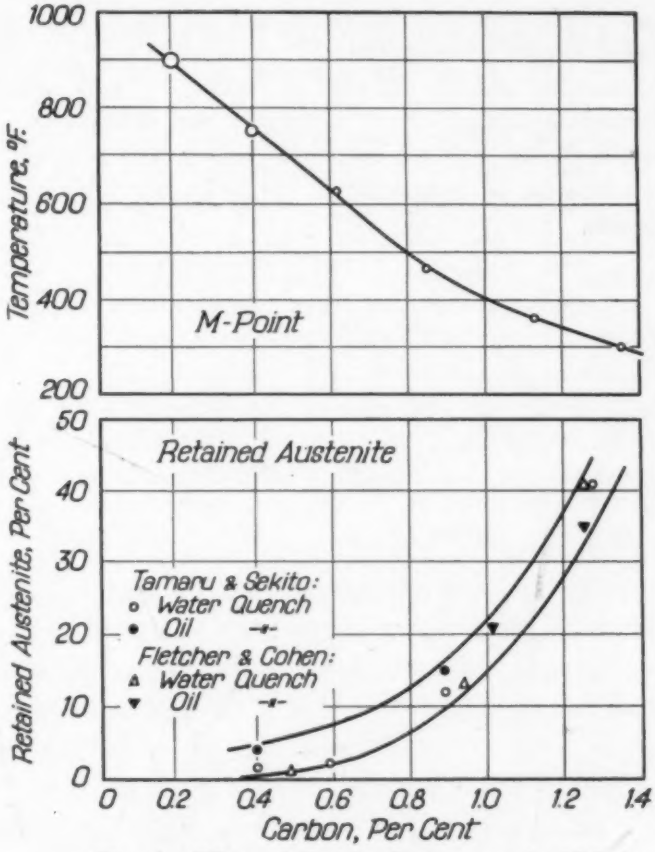


Fig. A—Effect of Carbon Content on the M-Point (21) and the Retained Austenite Content (11).

but rather on the extent of this transformation per degree drop in temperature. For example, two steels with the same M-point will not contain equal amounts of retained austenite if they happen to have different rates of austenite decomposition with respect to the dropping temperature. As a matter of fact, in the high-carbon range the amount of retained austenite increases with the carbon content at a much faster pace than the decreasing M-point would indicate.

The austenite contents reported here are in reasonably good agreement with published values. Perfect coincidence is not to be expected because of variations from heat to heat, differences in specimen geometry, and uncertainties in previous methods of measurement. Fig. A shows that the authors' values and those of Tamaru and Sekito[17] fall within a fairly narrow scatter

[17]Reference 11 in paper.

band. The potent effect of carbon in the high carbon range is evident, and does not correspond with the M-point curve.

The austenitizing time used in this work was 30 minutes, and was sufficient to attain complete carbide solution at the austenitizing temperatures selected. The absence of undissolved carbides was checked metallographically with the special etching reagents referred to by Mr. Rose as well as with the usual reagents. Furthermore, the lattice parameters of both the martensite and austenite also indicated complete solution of the carbides. However, even with undissolved carbides in the structure, no significant change in the mechanism of the tempering process would be expected.

The rate of quenching beyond the critical cooling velocity seems to affect the amount of retained austenite, but no generalization appears possible at the present time. Both water and oil-quenched values are plotted in Fig. A. Here again, the mechanism of tempering is the same for both the water and oil-quenched specimens.

# THE TEMPERING OF NICKEL AND NICKEL-MOLYBDENUM STEELS

By Dara P. Antia and Morris Cohen

*Abstract*

*In this paper, it is demonstrated that nickel and nickel-molybdenum steels, containing 0.4 to 1.0 per cent carbon and alloy contents typical of commercial heat-treating grades, pass through the same three stages of tempering as do the plain carbon steels. These stages correspond to the following phase changes: (a) decomposition of the tetragonal martensite, (b) decomposition of the retained austenite, and (c) formation of cementite.*

*Both carbon and nickel enhance the retention of austenite in the hardened structure, but molybdenum causes a slight decrease in the amount of austenite. The stabilizing influence of nickel on the austenite during tempering is rather small, and that of carbon and molybdenum is even less so. The retained austenite decomposes either isothermally or on heating to the tempering temperature, unlike the case of certain other alloy steels in which the decomposition occurs mainly on cooling from the tempering temperature.*

RECENT studies (1-3)* have shown that hardened plain carbon steels undergo three important phase changes on tempering. These may be summarized as follows: (a) the decomposition of the tetragonal martensite into ferrite and a transition precipitate, (b) the decomposition of the retained austenite into an acicular structure with the same state of aggregation as the tempered martensite, and (c) the conversion into cementite of the transition precipitate formed during (a) and (b). The present paper describes the effect of nickel, with and without molybdenum, on these three stages of tempering.

The compositions selected for investigation contain 3.6 and 4.8 per cent nickel with 0.4 to 1.0 per cent carbon and 0 to 0.5 per cent

*The figures appearing in parentheses refer to the bibliography appended to this paper.

This paper is based on a thesis submitted by Dara P. Antia in partial fulfillment of the requirements for the degree of Doctor in Science at the Massachusetts Institute of Technology.

A paper presented before the Twenty-fifth Annual Convention of the Society, held in Chicago, October 18 to 22, 1943. Of the authors, Dara P. Antia is research assistant and Morris Cohen is associate professor of physical metallurgy, Massachusetts Institute of Technology, Cambridge, Mass. Manuscript received July 6, 1943.

molybdenum. In view of their relatively high carbon contents, most of the steels do not correspond to the regular commercial nickel and nickel-molybdenum grades, but they are quite worthy of scientific investigation because of the comparatively large quantities of austenite which they retain in the hardened condition. At the same time, the high-carbon compositions do have practical significance inasmuch as they resemble the chemistry existing in the hardened case of carburizing steels, such as S.A.E. 2315, 2515, and 4815. The service properties of these carburized steels are greatly influenced by the amount of austenite retained in the high-carbon case and by the subsequent structural changes which occur during tempering.

## Previous Work

Despite the extensive literature on nickel and nickel-molybdenum steels (4), very few investigations have been applied to the compositions used for the present research. Eash and Pilling (5) have developed structural diagrams for cast nickel steels containing up to 4 per cent carbon and 30 per cent nickel. Davenport (6) has studied the action of nickel and molybdenum on the kinetics of isothermal austenite decomposition, and Bain (7) has summarized the effect of these elements on the eutectoid composition and temperature. The rate of diffusion of carbon in austenite has been shown by Wells and Mehl (14) to increase in the presence of nickel, but the effect is inappreciable for the amount of nickel ordinarily found in heat-treating or carburizing steels.

The work of Zyuzin, Sadovski and Baranchuk (8) dealing with the influence of alloying elements on 1 per cent carbon steel indicates that nickel and molybdenum lower the martensite point and increase the amount of retained austenite, but exert only a slight stabilizing effect compared to manganese, chromium and silicon on the retained austenite during tempering. Gardner, Cohen and Antia (9) have shown that the austenite content in hardened 5 per cent nickel steels depends greatly on the carbon content and the quenching rate. Using the X-ray method developed by these authors for the quantitative determination of retained austenite, Freedman (10) found that large amounts of austenite may be retained in case-carburized nickel steels.

## Experimental Details

*Preparation of Steels and Specimens*—The steels were melted

in 140-pound induction furnace heats and poured into 30-pound hot-topped ingots. After each cast, further alloy additions were made to the remaining bath so that the ingots formed a systematic series of compositions. The chemical analyses are given in Table I.

**Table I**
**Chemical Analyses**

| Steel No. | Per Cent by Weight | | | | |
|---|---|---|---|---|---|
| | C | Mn | Si | Ni | Mo |
| 1 | 0.38 | 0.58 | 0.54 | 4.76 | .... |
| 2 | 0.62 | 0.52 | 0.54 | 4.76 | .... |
| 3 | 0.81 | 0.52 | 0.54 | 4.76 | .... |
| 4 | 1.00 | 0.43 | 0.01 | 4.82 | .... |
| 5 | 1.00 | 0.45 | 0.01 | 3.63 | .... |
| 6 | 0.74 | 0.52 | 0.25 | 3.58 | .... |
| 7 | 0.75 | 0.52 | 0.25 | 3.58 | 0.24 |
| 8 | 0.74 | 0.52 | 0.25 | 3.58 | 0.47 |

In all cases, the sulphur and phosphorus contents were under 0.05 per cent. It will be noted that steels 1 through 4 constitute a series of 4.8 per cent nickel compositions with variable carbon, while steels 6 through 8 contain constant carbon and nickel with variable molybdenum. Comparison of steels 4 and 5 should show the effect of 3.6 versus 4.8 per cent nickel at the 1 per cent carbon level, whereas steels 5 and 6 should contribute some idea of the effect of carbon content at the 3.6 per cent nickel level.

The ingots were initially forged approximately round with little reduction in cross section, and turned down on a lathe until only clean metal was obtained. After the hot tops were cropped, the remaining stock (approximately 3 inches in diameter) was forged into ⅞-inch square and ½-inch round bars. All the steels underwent appreciable hardening on air cooling from the forging operation, and annealing was necessary to facilitate the subsequent machining. An annealing temperature of 1400 degrees Fahr. (760 degrees Cent.) was found to be satisfactory, except for steels 3 and 4 containing 0.81 and 1.00 per cent carbon with 4.8 per cent nickel. In order to avoid graphitization in these two steels, the annealing temperature had to be lowered to 1200 degrees Fahr. (650 degrees Cent.) and 1050 degrees Fahr. (565 degrees Cent.) respectively. After annealing, the ⅞-inch square bars were machined into ½×½×⅝-inch specimens, and the ½-inch round bars into 0.240-inch diameter by 4¼-inch rods.

*Heat Treatment*—The specimens were austenitized for ½ hour at 1700 degrees Fahr. (925 degrees Cent.) in a carbonaceous

muffle, and were then quenched into oil. All of the carbides were completely dissolved by this treatment. As a general rule, the hardened specimens were kept at room temperature for about 24 hours before tempering. The tempering experiments were of three types: (a) Dilatometric and magnetic studies were carried out during continuous heating to 1000 degrees Fahr. (540 degrees Cent.) at a rate of 5 degrees Fahr. (2.8 degrees Cent.) per minute. (b) Dilatometric and magnetic measurements were also conducted "at temperature" during isothermal tempering runs. (c) Other iso-

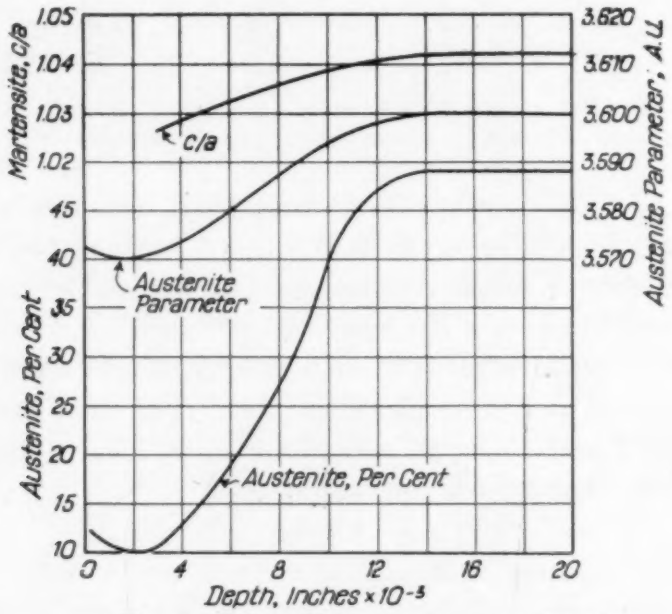


Fig. 1—X-Ray Measurements as a Function of Depth in Hardened 1.0 Per Cent Carbon, 4.8 Per Cent Nickel Steel. Oil-Quenched from 1700 Degrees Fahr.

thermal runs were interrupted periodically by cooling to room temperature for X-ray, specific volume and hardness measurements. The temperature control was usually better than ±5 degrees Fahr.

*Types of Measurements*—The dilatometric and magnetic determinations were made simultaneously on the 0.240×4¼-inch rod specimens in apparatus developed for such tempering studies by Zmeskal and Cohen (11). The ½×½×⅝-inch specimens were used for the X-ray, specific volume and hardness measurements. Retained austenite contents were ascertained after hardening and during tempering by the X-ray method of Gardner, Cohen and Antia (9). Other details of the above measurements are described elsewhere (1), (12).

Despite the carbonaceous muffle employed for the austenitizing treatments, enough decarburization invariably occurred to reduce the retained austenite content at the surface of the specimens, as well as to lower the lattice parameters of the austenite and co-existing martensite. As indicated in Fig. 1, these decarburization effects extended to a depth of about 0.014 inch. In order to prevent such extraneous factors from entering into the tempering experiments, the usual practice was to remove at least 0.040 inch by careful grinding and electrolytic etching after the hardening operation. This precaution was only necessary for the surfaces to be used for the X-ray and hardness measurements. The loss of carbon was too small, compared to the specimen-bulk, to affect the dilatometric, magnetic and specific volume determinations.

## Discussion of Results

The amounts of retained austenite in the eight steels under discussion are listed in Table II. There is a marked tendency for

**Table II**
**Retained Austenite Contents and Lattice Parameters After Oil Quenching From 1700 Degrees Fahr. (925 Degrees Cent.)**

| Steel No. | Composition C | Ni | Mo | Per Cent Retained Austenite* Sample Size ½x½x⅝" | 4¼x.24" Diameter | Austenite Parameter A.U. | Martensite Axial Ratio |
|---|---|---|---|---|---|---|---|
| 1 | 0.38 | 4.76 | .... | 3 | <3 | 3.575 | ..... |
| 2 | 0.62 | 4.76 | .... | 8 | 6 | 3.586 | 1.027 |
| 3 | 0.81 | 4.76 | .... | 20 | 23 | 3.593 | 1.035 |
| 4 | 1.00 | 4.82 | .... | 48 | 37 | 3.600 | 1.042 |
| 5 | 1.00 | 3.63 | .... | 37 | 27 | 3.599 | 1.041 |
| 6 | 0.74 | 3.58 | .... | 14 | 11 | 3.587 | 1.031 |
| 7 | 0.75 | 3.58 | 0.24 | 13 | 9.5 | 3.591 | 1.030 |
| 8 | 0.74 | 3.58 | 0.47 | 12 | 9 | 3.592 | 1.032 |

*From X-ray intensity measurements (9).

the cube-shaped specimens to retain more austenite than the rod-shaped specimens even though both sizes harden completely as a result of oil quenching*. While this phenomenon was not investigated further, it is tentatively believed to be related to the complex dependence of quenching and transformation stresses on the geometry of the specimen and the rate of cooling. In any event, a comparison of the data in Table II reveals that both

*Oil quenching of these alloy steels was sufficiently rapid to suppress the formation of pearlite, bainite or proeutectoid constituents.

carbon and nickel are effective in retaining austenite, with the carbon being more potent. For example, between 0.6 and 1 per cent carbon at the 4.8 per cent nickel level, there is an increase of about 9 per cent of retained austenite for each addition of 0.1 per cent carbon, whereas, at the 1 per cent carbon level between 3.6 and 4.8 per cent nickel, there is an increase of about 0.9 per cent of austenite for each addition of 0.1 per cent nickel. Molyb-

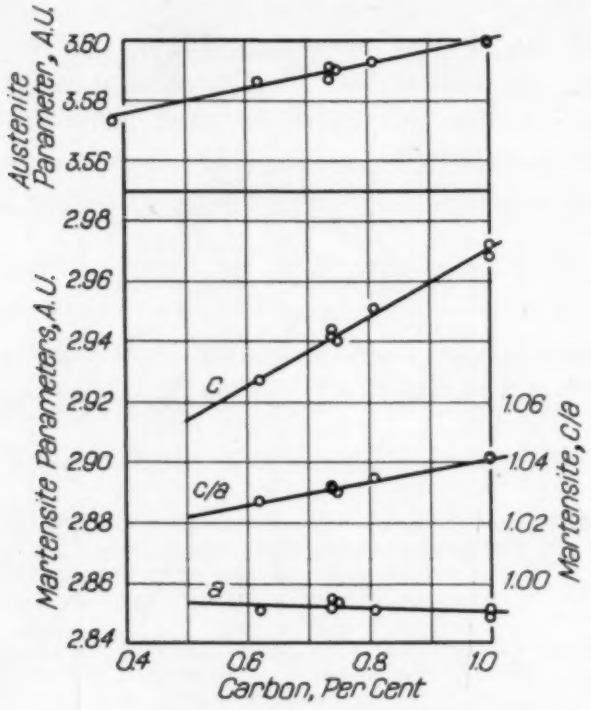


**Fig. 2—Relationship Between Lattice Parameters and Carbon Content in Steels Containing up to 5 Per Cent Nickel and up to 0.5 Per Cent Molybdenum.**

denum, on the other hand, actually causes a slight decrease in the amount of austenite.

Table II also presents the lattice constants for these steels in the hardened condition. Both the austenite and martensite parameters are primarily dependent on the carbon content, and are comparatively insensitive to nickel and molybdenum up to the amounts used. Fig. 2 shows the austenite and martensite parameters as a function of the carbon content.

Figs. 3 and 4 illustrate the dilatometric and magnetic changes that take place on continuous heating of the hardened steels at a constant rate of 5 degrees Fahr. (2.8 degrees Cent.) per minute. These curves exhibit the same three stages of tempering that

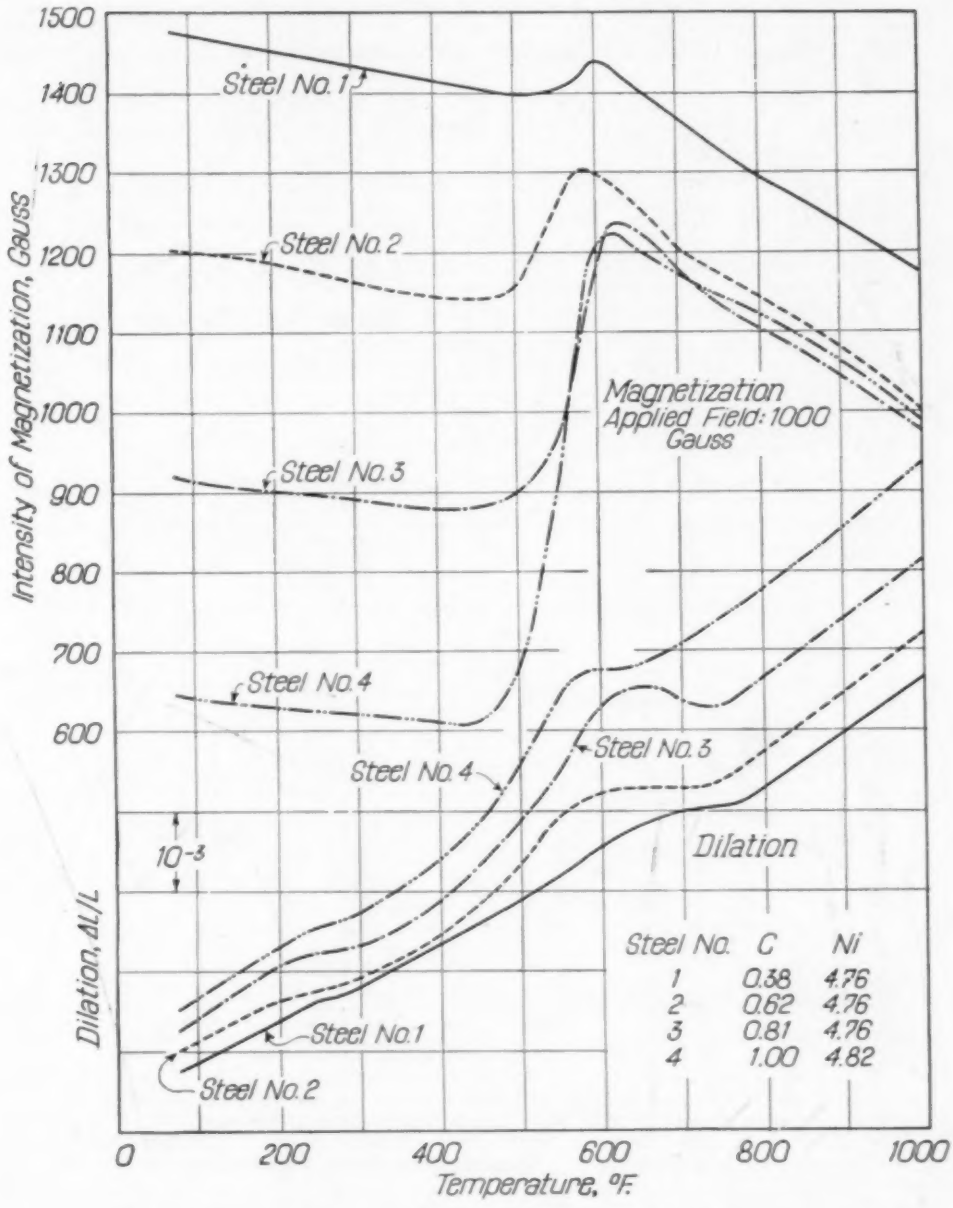


**Fig. 3—Magnetization and Dilation Curves on Continuous Heating of 4.8 Per Cent Nickel Steels After Oil Quenching from 1700 Degrees Fahr. (925 Degrees Cent.). Heating Rate: 5 Degrees Fahr. Per Minute. Displacement Between Dilation Curves is Arbitrary.**

prevail in plain carbon steels (1), (2). In the temperature range between 200 and 325 degrees Fahr. (95 and 165 degrees Cent.), the first stage is shown by the contractions which are impressed on the dilation curves, but there is little, if any, corresponding change in magnetization. On heating beyond 450 degrees Fahr. (230 degrees Cent.), however, the steels undergo a striking increase in magnetization along with a notable increase in length.

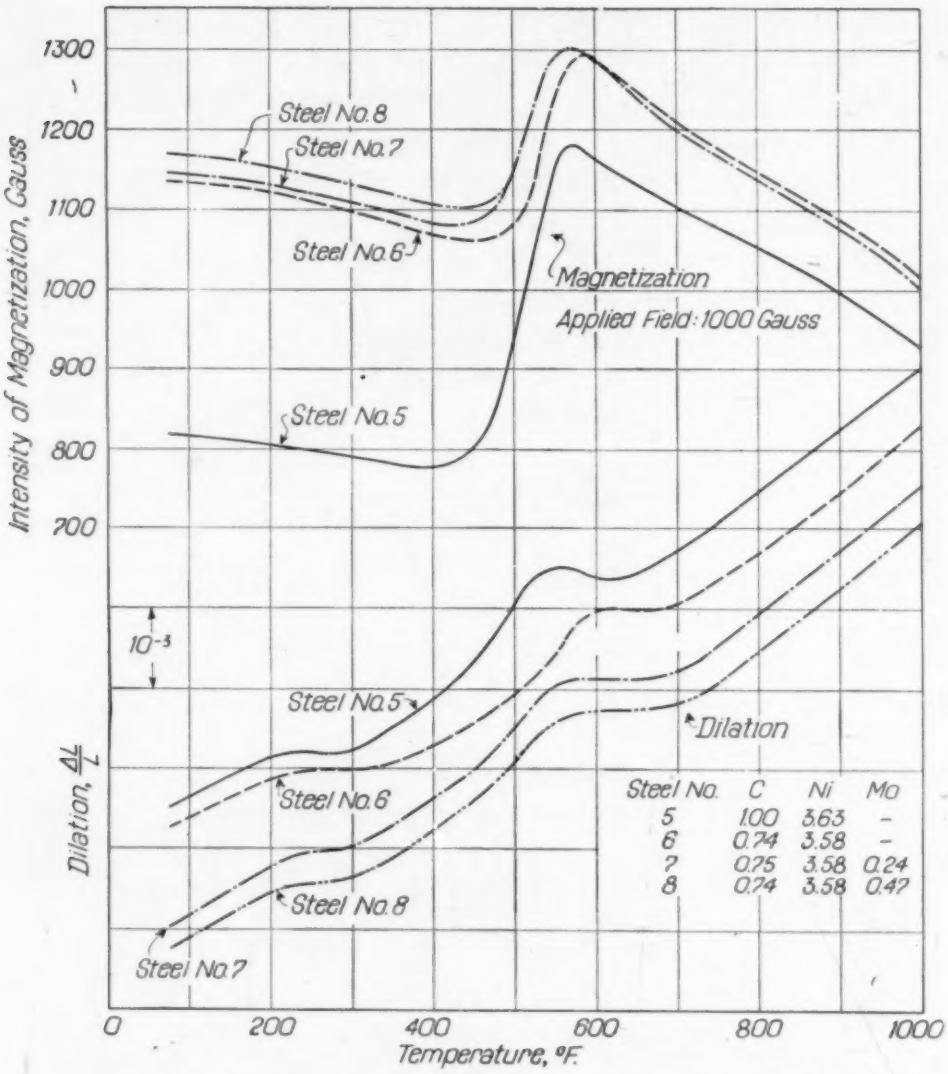


**Fig. 4—Magnetization and Dilation Curves on Continuous Heating of 3.6 Per Cent Nickel Steels With and Without Molybdenum After Oil Quenching from 1700 Degrees Fahr. (925 Degrees Cent.). Heating Rate: 5 Degrees Fahr. Per Minute. Displacement Between Dilation Curves is Arbitrary.**

This second stage continues to a temperature of 625-650 degrees Fahr. (330-345 degrees Cent.) where the third stage begins to predominate, the latter superimposing decreases in both magnetization and dilation on the normal temperature-dependent curves up to a temperature of approximately 750 degrees Fahr. (400 degrees Cent.). It is evident from Figs. 3 and 4 that the above tempering effects are basically the same for all the steels investigated although, of course, there are variations in the intensity of the different stages and the extent to which they overlap.

The kinetics of the three tempering stages are indicated by

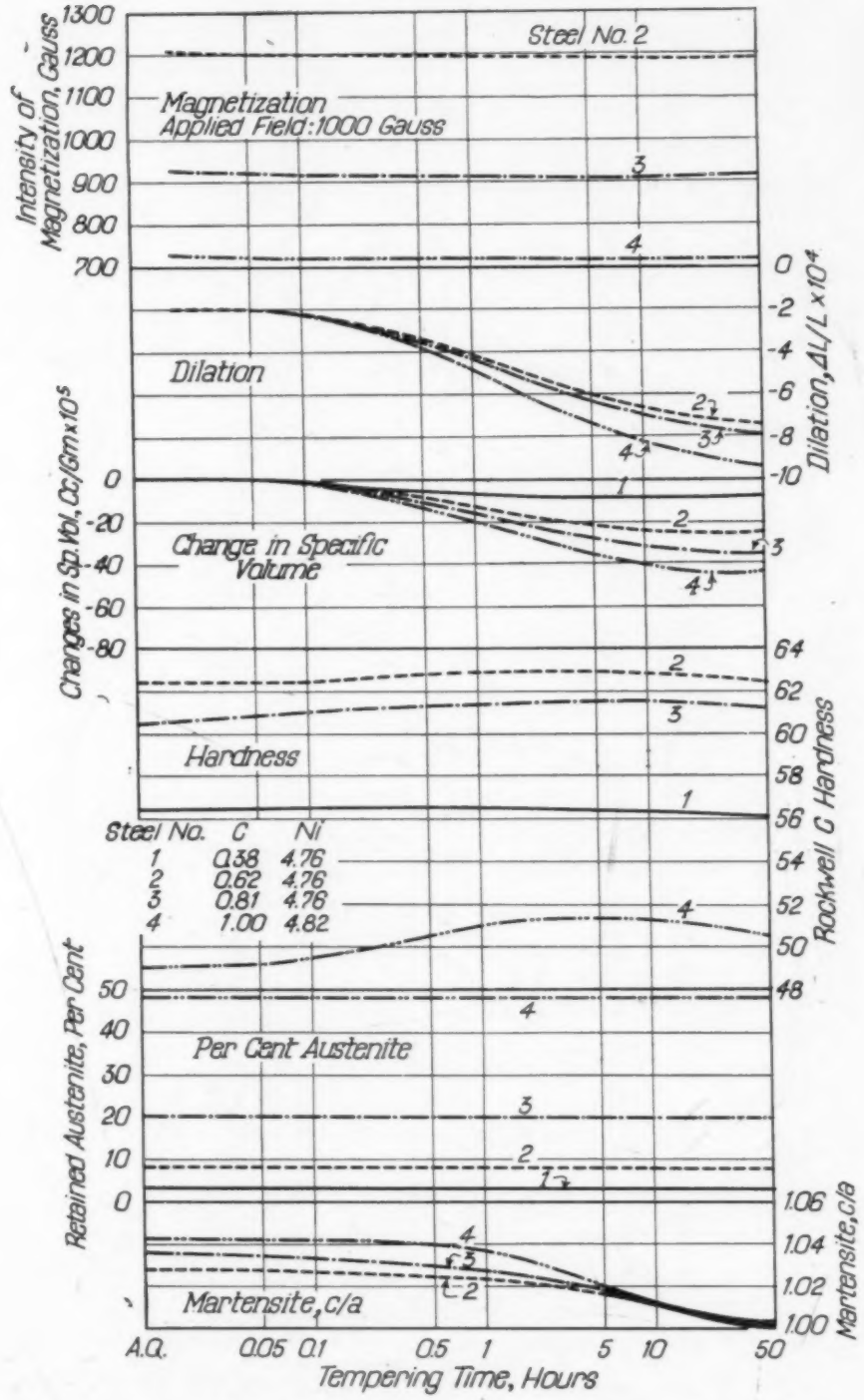


Fig. 5—Effect of Tempering Time at 200 Degrees Fahr. (95 Degrees Cent.) on 4.8 Per Cent Nickel Steels After Oil Quenching from 1700 Degrees Fahr. (925 Degrees Cent.).

the isothermal measurements in Figs. 5 to 8. On tempering at 200 degrees Fahr. (95 degrees Cent.) (Fig. 5), the first stage develops slowly with a gradual contraction in both length and

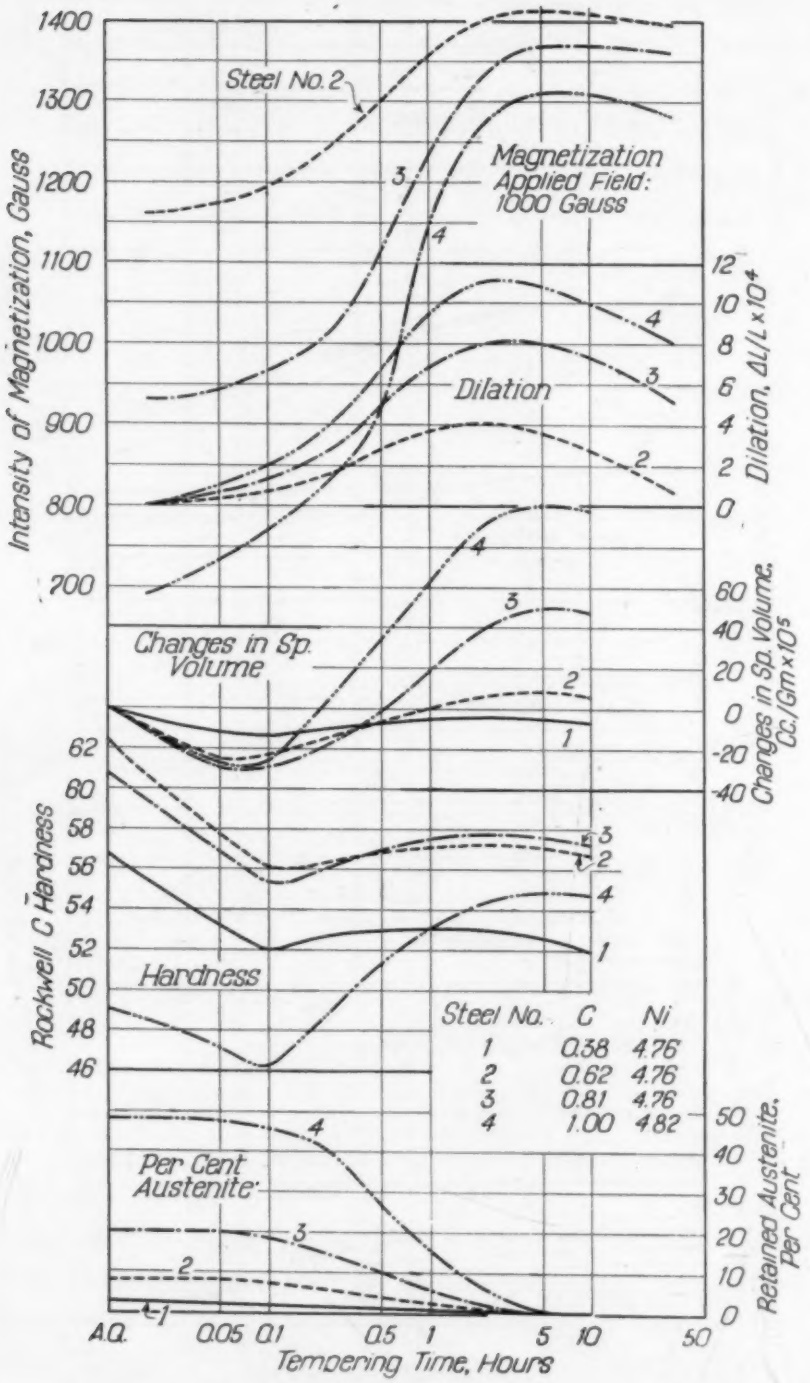


**Fig. 6—Effect of Tempering Time at 500 Degrees Fahr. (260 Degrees Cent.) on 4.8 Per Cent Nickel Steels After Oil Quenching from 1700 Degrees Fahr. (925 Degrees Cent.).**

volume, while the magnetization drops off almost imperceptibly. During this time, the axial ratio of the tetragonal martensite approaches unity, but the austenite remains constant in amount as

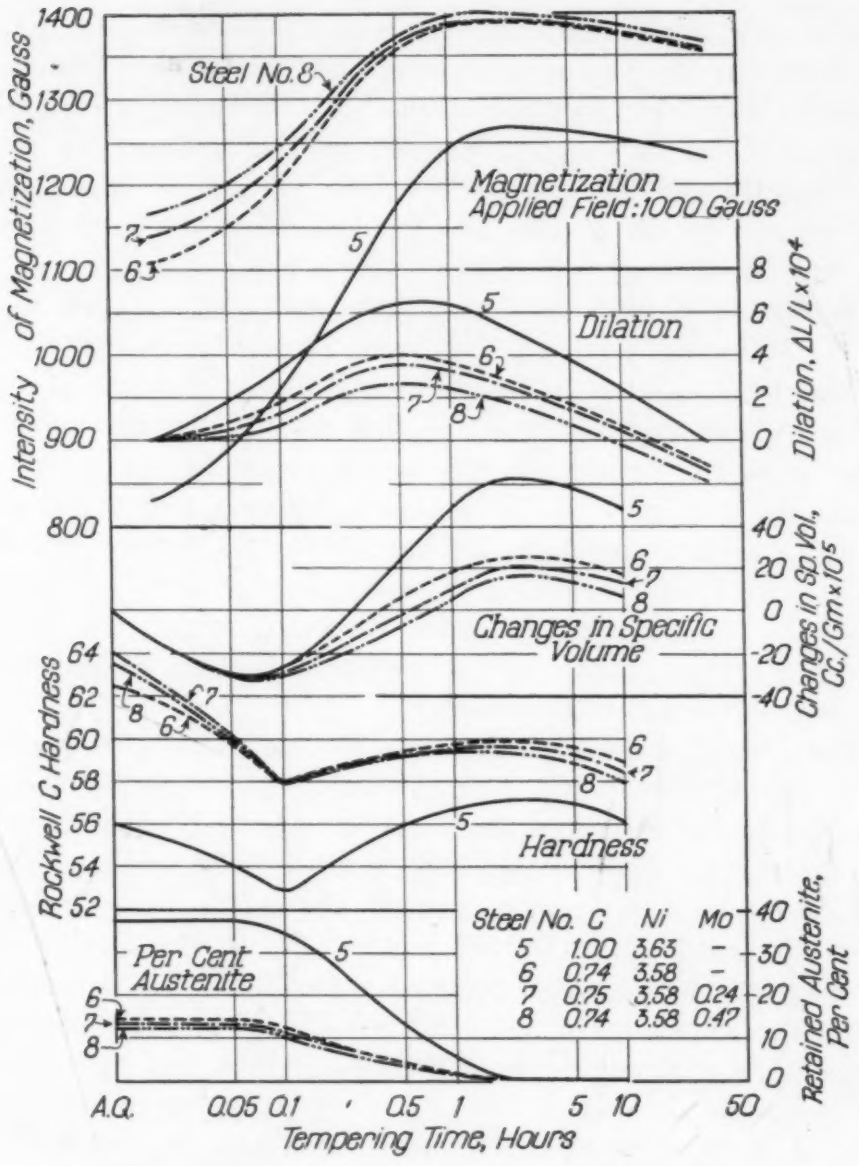


**Fig. 7—Effect of Tempering Time at 500 Degrees Fahr. (260 Degrees Cent.) on 3.6 Per Cent Nickel Steels With and Without Molybdenum After Oil Quenching from 1700 Degrees Fahr. (925 Degrees Cent.).**

well as in composition*. Obviously, then, the first tempering stage involves the disappearance of the tetragonal martensite, and the decomposition product is undoubtedly the same aggregate of ferrite and transition precipitate that was previously reported by the authors for plain carbon steel (1).

Like the plain carbon grades (2), the nickel steels gain in

*No change in lattice parameter of the retained austenite was observed during any of these tempering experiments.

hardness as a result of the martensite decomposition (Fig. 5). The extent of the hardening increases with the carbon content, although the initial hardness diminishes with increasing carbon beyond 0.6 per cent due to the progressively greater amounts of retained austenite. During the later part of the martensite decomposition, the hardness begins to fall off, but the effect is quite small on tempering at 200 degrees Fahr. (950 degrees Cent.).

When the tempering temperature is raised to 500 degrees Fahr. (260 degrees Cent.) (Figs. 6 and 7), the hardening associated with the break-up of the martensite is entirely obscured by the subsequent softening. In fact, the first tempering stage takes place so quickly that the attendant contraction occurs before the dilatometer can be stabilized at the tempering temperature. Hence, the first stage contraction does not appear in the dilation curves of Figs. 6 and 7. However, this contraction is nicely detected by the specific volume measurements since the latter can be made leisurely at room temperature after rapid heating to and cooling from the tempering treatments.

The second stage of tempering sets in after a few minutes at 500 degrees Fahr. (260 degrees Cent.), and is characterized by increases in magnetization, hardness, length and volume. All of these changes are due to the isothermal decomposition of the retained austenite, and their magnitude depends on the amount of austenite present in the hardened steel. As shown by the X-ray intensity determinations, the retained austenite begins to decompose at about the same time in all the steels. However, the stability of the austenite, as measured by the time for complete disappearance of the austenite diffraction lines, is affected by the nickel content. In the 4.8 per cent nickel steels, about 5 hours at 500 degrees Fahr. (260 degrees Cent.) are required for the complete conversion of the retained austenite, whereas in the 3.6 per cent nickel series, only 2 hours are necessary. Despite the austenite-retaining power of carbon, the stability of the austenite on tempering is not materially altered by wide variations in the carbon content. Furthermore, the kinetics are hardly influenced by the presence of molybdenum up to 0.5 per cent (Fig. 7). In no case was any consistent change in composition (lattice parameter) of the austenite observed either before or during its decomposition.

The rate of austenite conversion goes up rapidly with the tempering temperature. At 600 degrees Fahr. (315 degrees Cent.)

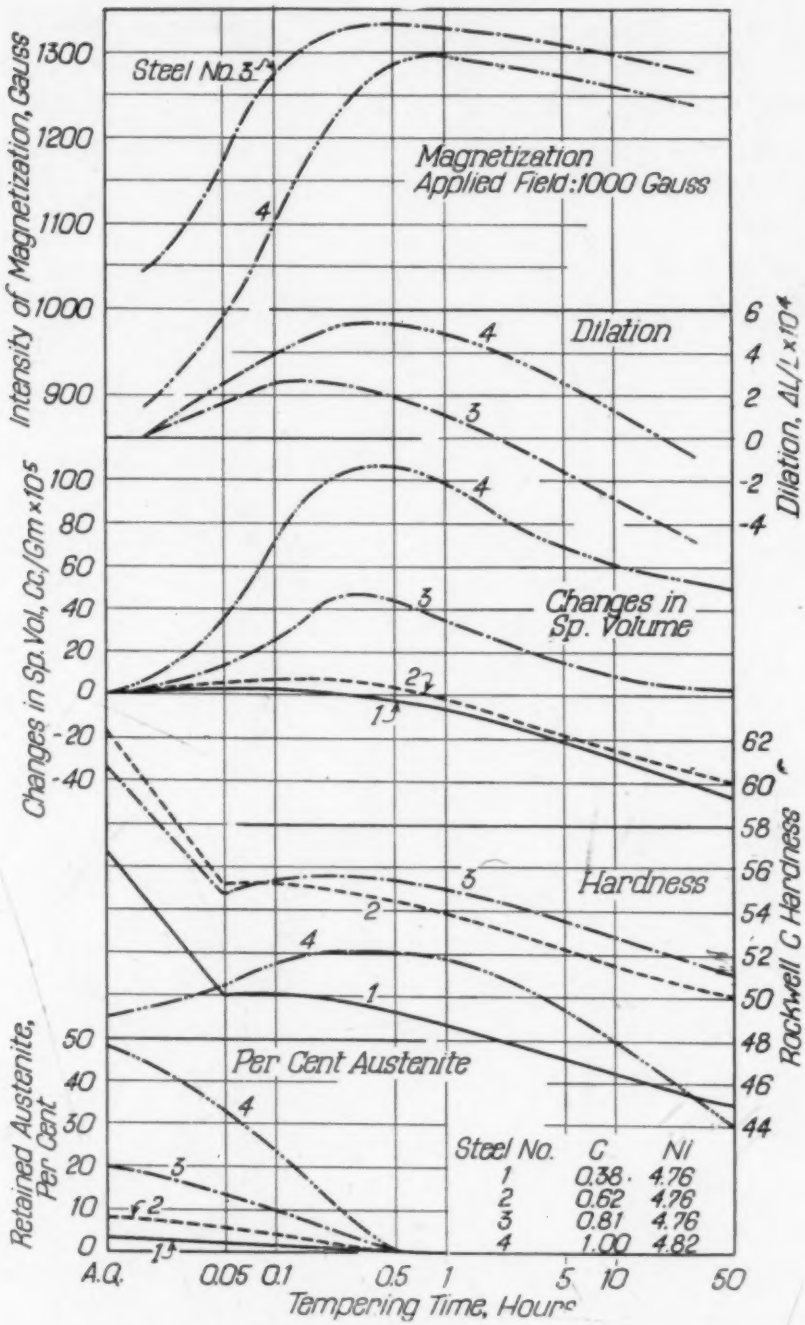


Fig. 8—Effect of Tempering Time at 600 Degrees Fahr. (315 Degrees Cent.) on 4.8 Per Cent Nickel Steels After Oil Quenching from 1700 Degrees Fahr. (925 Degrees Cent.).

(Fig. 8), the austenite disappears in only ½ hour in the 4.8 per cent nickel steels. The subsequent drop in the magnetization, dilation and specific volume curves marks the third stage of tempering, and has been demonstrated to be due to the transformation into cementite of the previously formed transition precipitate (1). This

phase transformation was confirmed in the present work. All of the steels displayed definite cementite Curie points on cooling at the end of the tempering runs at 600 degrees Fahr. (315 degrees Cent.) (32 hours), but after the tempering runs at 500 degrees Fahr. (260 degrees Cent.) (32 hours) the Curie points were quite weak.

It is interesting to note from the heating curves of Figs. 3 and 4 that the third stage occurs about 75 degrees Fahr. (42 degrees Cent.) higher in these alloy steels than in straight carbon steels (2), but there is hardly any difference when the first stages are compared. These two facts may be related in the following way. Since nickel and molybdenum in the amounts used do not appreciably retard the decomposition of the martensite on tempering, it is reasonable to believe that the ferrite and transition precipitate each contain almost the same statistical distribution of nickel and molybdenum atoms as existed in the original martensite. Accordingly, when cementite forms during the third stage, diffusion must provide for the proper partition of the nickel and molybdenum between the ferrite and the carbide phase. In all probability, there is at least a partial migration of nickel to the ferrite and of molybdenum to the cementite. The need for such diffusion, not encountered in the straight carbon steels, might well explain the higher third-stage temperature range exhibited by the alloy steels.

Thus, the mechanism of tempering at play in the nickel and nickel-molybdenum steels is quite similar to that in the plain carbon steels. The three stages of tempering are time-dependent as well as temperature-dependent. In particular, it should be emphasized that the retained austenite decomposes on heating to, or holding at the tempering temperature. In this respect, the alloy steels under discussion are unlike high speed steels (12), which undergo retained austenite transformation on cooling from the tempering temperature. The difference in behavior appears to be primarily a matter of austenite stability, since in high-carbon high-chromium steels, the retained austenite may be made to transform either on heating to, or on holding at, or on cooling from the tempering temperature, depending on the extent of alloy-carbide solution achieved during the austenitizing treatment (13). Hence, although nickel is very effective in retaining austenite, its stabilizing action on tempering is comparatively small. Furthermore, while carbon is even more powerful than nickel in retaining austenite, its stabilizing effect on tempering is even less.

The decomposition of the retained austenite in the nickel and nickel-molybdenum steels results in appreciable secondary hardening (Figs. 6-8), but the simultaneous softening of the tempered martensite prevents the attainment of hardness values over Rc 60. In other words, when the steels are initially soft due to the presence of retained austenite, tempering through the second stage to convert the austenite does not develop the high hardness which would be expected if the austenite were not retained in the first place. This dilemma is also encountered in carburized nickel and nickel-molybdenum steels when excessive amounts of austenite are retained. According to the data presented, the situation cannot be corrected by tempering. In such cases, subatmospheric cooling may be employed to minimize the amount of retained austenite, followed by tempering through the first stage in the usual way.

## Conclusions

1. Carbon and nickel promote the retention of austenite in hardened steel, but the carbon is much more effective. In these nickel steels, molybdenum up to 0.5 per cent (even though in solution) causes a slight decrease in the amount of retained austenite.

2. Nickel has a definite, but relatively slight, stabilizing influence on the retained austenite during tempering. Carbon up to 1 per cent and molybdenum up to 0.5 per cent have very little effect on the stability of the retained austenite in these steels.

3. The nickel and nickel-molybdenum steels display three stages of tempering, essentially the same as has been found for plain carbon steels.

4. The retained austenite in these steels decomposes either isothermally or on heating to the tempering temperature. There is no evidence of austenite decomposition on cooling from the tempering temperature, such as occurs in high speed steel.

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## DISCUSSION

PETER PAYSON:[1] I have been very much interested in these papers because the dark etching hence poorly corrosion resistant condition which the authors describe as the transition phase reminds me that some twelve years ago I suggested a similar incipient precipitation was responsible for the poor corrosion resistance in the grain boundaries of 18-8 which had been given the so-called sensitized treatment. I should add that I hope this transition phase suggested by Dr. Cohen and his associates is more widely accepted by metallurgists than mine was.

I would like to make one suggestion and ask two questions. The suggestion is that we resurrect the term troostite and apply it to the transition phase. We abandoned troostite some seven or eight years ago because we could not at that time satisfactorily differentiate between troostite and sorbite. Now apparently we can distinguish between them, troostite being the stage of tempered martensite prior to the separation of the carbides, and sorbite the stage after the carbides are present.

The questions I would like to ask are these:

First, since we know that austenite when it transforms to martensite does not change all at once to a single product, but rather changes gradually over a range of temperatures to a series of products, is the tetragonality of the martensite attributable to the fact that some of the martensite formed at 400, and some

[1]Chief research metallurgist, Crucible Steel Company of America, Harrison, N. J.

at 350, and some at 300 degrees Fahr. (205, 175 and 150 degrees Cent.), and so forth, and that the martensite formed at 400 degrees Fahr. (205 degrees Cent.) has a slightly different parameter from that formed at 300 degrees Fahr. (150 degrees Cent.) and both of these are different from that formed at 100 degrees Fahr. (38 degrees Cent.)?

The second question is, is it possible that the minimum on the impact curve between the impact value and tempering temperature in low alloy constructional steels which occurs at about 600 to 650 degrees Fahr. (315 to 345 degrees Cent.), is caused by the presence of the transition phase or troostite? We have so far had no satisfactory explanation for this phenomenon when steel is tempered at these temperatures. For the low carbon steels in which this phenomenon occurs, Dr. Cohen's data indicate the amount of retained austenite as insufficient to explain the low impact value by the transformation of the slight amount of retained austenite that might take place during this tempering around 600 or 650 degrees Fahr. (315 or 345 degrees Cent.). Now we have at least a coincidence of the facts that the notch impact remains low during the presence of the transition phase and that the impact value improves rapidly as the third stage of tempering proceeds.

### Authors' Reply

Mr. Payson's remarks are very welcome. Much has been said concerning the nomenclature of tempered steel structures, but the matter still remains confused. Obviously, it is difficult to arrive at sound terminology if little is known about the items that are to be named. We are now beginning to acquire a rational basis for defining as well as naming the tempered states, and in the light of the present work, the distinction between troostite and sorbite as proposed by Mr. Payson appears quite reasonable. When the time seems appropriate, we shall be very glad to join with Mr. Payson and others in an attempt to attain some general agreement on the subject.

In his first question, Mr. Payson asks whether the tetragonality of martensite can be attributed to a variable parameter caused by the fact that the martensite forms progressively over a range of temperatures. Such an explanation is invalid on at least three counts.[2] If the lattice parameter of quenched martensite were simply variable, and not truly tetragonal, the martensite diffraction lines would be broad, but not resolvable into doublets. Yet, the doublets are clearly observed.[3] There is no evidence that the tetragonality of martensite is materially affected by its temperature of formation. The axial ratio is primarily a function of the dissolved carbon content, and if the latter is uniform, there is no noticeable difference in the tetragonality of the martensite produced at different temperatures on cooling.[4] Martensitic reactions in carbon-free iron-nickel alloys[3] and in certain nonferrous alloys[3, 4] do not result in tetragonal structures.

[2]A. B. Greninger and A. R. Troiano, "Crystallography of Austenite Decomposition," *Transactions*, American Institute of Mining and Metallurgical Engineers, Vol. 140, 1940, p. 307.

[3]A. B. Greninger and V. G. Mooradian, "Strain Transformation in Metastable Copper-Zinc and Beta Copper-Tin Alloys," *Transactions*, American Institute of Mining and Metallurgical Engineers, Vol. 128, 1938, p. 337.

[4]A. B. Greninger, "The Martensite Transformation in Beta-Copper, Copper-Aluminum Alloys," *Transactions*, American Institute of Mining and Metallurgical Engineers, Vol. 133, 1939, p. 204.

In other words, a martensitic product that forms characteristically on cooling does not necessarily have a tetragonal structure. Consequently, if the latter is found, as in the case of steel, the tetragonality cannot be accounted for by the cooling nature of the transformation.

We have not studied the tempering of the low alloy constructional steels mentioned by Mr. Payson in his second question, and hence are not in a position to offer any specific explanation of the minimum in the impact-tempering curves of these materials. However, the indications are that the magnitude of the dip in the curves increases with the amount of retained austenite present in the quenched steel. Therefore, one tends to suspect that the phenomenon is associated with the decomposition of the retained austenite, even though the amount of austenite involved is relatively small. At the same time, the martensite decomposition product probably also plays a role in this phenomenon. Even when there is practically no retained austenite in the hardened steel, the impact strength remains relatively low on tempering up to about 650 degrees Fahr. (345 degrees Cent.), and then a striking improvement begins to set in.[5] This change appears to coincide with the conversion of the transition precipitate into cementite. It is not yet known whether, or to what extent, the formation of alloy carbides enters into this picture. An investigation of alloy carbide precipitation is on our program.

[5]M. A. Grossmann, "Principles of Heat Treatment," published by the American Society for Metals, 1935, p. 79.

# CREEP STRENGTH, STABILITY OF MICROSTRUCTURE AND OXIDATION RESISTANCE OF CR-MO AND 18 CR-8 NI STEELS

By R. F. Miller, W. G. Benz and M. J. Day

*Abstract*

*Investigation of the effect of heat treatment on creep strength and stability of microstructure of several chromium-molybdenum and chromium-nickel steels, at 1000 and 1100 degrees Fahr., over a period of 3000 hours showed that at 1100 degrees Fahr. the creep strength of the Cr-Mo steels is substantially the same over the range 2 to 9 per cent chromium, that of 5 Cr-Mo steel is increased by addition of titanium or columbium, and that of 18 chromium-8 nickel with columbium is greater than for 18-8 with titanium or 18-8 itself.*

*A period of 3000 hours at 900 degrees Fahr. produced no observable change of microstructure except in pearlitic C-0.50 Mo steel, but at 1000 degrees Fahr. there was a marked change in all the C-Mo steels; chromium stabilizes the structure, little or no change being visible in the Cr-Mo steels after 3000 hours at 1100 degrees Fahr.*

*The resistance to oxidation of the C-Mo steels in air for 1000 hours at 1100 and 1400 degrees Fahr. was about the same as that of plain carbon steel, and was not appreciably improved by chromium up to 3 per cent or silicon up to 0.75 per cent; further increase of chromium or silicon content was beneficial. At 1700 degrees Fahr. all the C-Mo steels and the Cr-Mo steels were severely attacked.*

DURING the past several years, an investigation of the effect of heat treatment on the creep strength of various C-Mo and Cr-Mo steels has been in progress, the results of which have been reported from time to time in the literature (1), (3), (4).* Several of the alloys which were originally tested in only one condition of heat treatment have now been tested in an alternative con-

*The figures appearing in parentheses pertain to the references appended to this paper.

A paper presented before the Twenty-fifth Annual Convention of the Society, held in Chicago, October 18 to 22, 1943. Of the authors, R. F. Miller and W. G. Benz are associated with the Research Laboratory, U. S. Steel Corp., Kearny, N. J., and M. J. Day is associated with the metallurgical division, Carnegie-Illinois Steel Corp., Chicago. Manuscript received June 8, 1943.

dition, and some previously tested only at 1000 degrees Fahr. (540 degrees Cent.) have now been tested at 1100 degrees Fahr. (595 degrees Cent.). The investigation has been further extended to include the steels 5 Cr-Mo-Cb-Si, 8 Cr-1 Mo, 8 Cr-1 Mo-Cb, and 9 Cr-1 Mo and some of the austenitic 18 Cr-8 Ni alloys.

Data on creep strength—that is, the stress for a creep rate of 1 millionth inch per inch per hour derived from tests lasting 3000 hours—are presented in Table III. It was found that at 1000 degrees Fahr. (540 degrees Cent.) the creep strength of air-cooled and tempered 2.25 Cr-1 Mo and 5 Cr-Mo steels was somewhat above that of the same materials in the furnace-cooled condition. Increase of chromium content from 2 to 9 per cent caused little change in *creep* strength at 1100 degrees Fahr. (595 degrees Cent.). The addition of titanium or columbium to 5 Cr-Mo steel increased its strength at 1000 and 1100 degrees Fahr., and addition of columbiun to 8 Cr-1 Mo steel increased its creep strength at 1100 degrees Fahr.

The creep strength of 18-8 at 1100 degrees Fahr. (595 degrees Cent.) is about the same as that of 18-8 Ti, that of 18-8 Cb is considerably higher, all of the materials being in the water-quenched or air-cooled condition. Stabilization of air-cooled 18-8 Ti and 18-8 Cb by heating for two hours at 1600 degrees Fahr. (870 degrees Cent.) caused a decrease in creep strength. These results are in general agreement with those of previous investigators (Table III).

The microstructure of the specimens was examined before and after creep testing. The results, combined with similar previous investigations (1), (3), were amplified by 3000-hour tempering tests at 900 and 1100 degrees Fahr., permitting a summary (Table V) of the structural stability of the alloys at 900, 1000, and 1100 degrees Fahr. No change occurred at 900 degrees Fahr. in any of the alloys except the air-cooled (pearlitic) C-0.5 Mo steel, in which a slight amount of spheroidization was apparent. At 1000 degrees Fahr., a marked change occurred in the air-cooled C-Mo steels, and a moderate change occurred in the air-cooled and tempered C-Mo steels. Addition of chromium appeared to stabilize the structure, little or no change being visible in the Cr-Mo steels at 1000 and 1100 degrees Fahr. Little or no change occurred at 1100 degrees Fahr. in the 18-8 materials, except in water-quenched 18-8, where grain boundary precipitation of carbides was apparent.

The amount of oxidation (scaling) of some of these steels has been reported in the literature (5), (6), (7), (8), (10), but

the data are fragmentary and uncorrelated, and the tests themselves generally of short duration. A new series of 1000-hour tests was therefore carried out by the gain-in-weight method, which has the double advantage of providing information on the relative rate of oxidation of the various alloys, and of eliminating the personal error involved in the loss-in-weight method. The results are shown in Table VI and Figs. 10 and 11. At 1100 and 1400 degrees Fahr. (595 and 760 degrees Cent.), the amount of oxidation of the C-Mo steels was about the same as that of plain carbon steel, and there was no appreciable improvement on addition of chromium up to about 3 per cent, or of silicon up to about 0.75 per cent. Addition of 5 per cent chromium was advantageous, and further increase of chromium content decreased the amount of oxidation, 27 Cr being the best material examined. Addition of 1.5 per cent silicon markedly lessened the amount of oxidation of Cr-Mo steels at 1100 and 1400 degrees Fahr. At 1700 degrees Fahr., the plain carbon, C-Mo, and 2 to 5 Cr-Mo steels oxidized completely within 1000 hours. The 18-8 materials were somewhat inferior to 27 Cr, and addition of columbium or titanium to 18-8 resulted in a slight decrease in amount of oxidation at 1700 degrees Fahr.

## Procedure and Results

### *Composition of Materials*

The composition of each of the steels is shown in Table I. The steels have been divided into several groups, the designations being the same as those employed in the previous publication (3) describing the results of creep tests on some of these steels. New designations have been assigned to materials not previously described. The six general groups are as follows:

### *General Groups of Steels under Investigation*

Group O—Plain carbon steel
" A—C-Mo steels
" B—1-3% Cr-Mo steels containing different amounts of Si
" C—5% Cr-Mo steels containing different amounts of Mo, Si, Ti, Cb and Al
" D—8-27% Cr or Cr-Mo steels
" E—18 Cr-8 Ni steels with and without Ti and Cb.

**Table I**
**Composition of Steels**

| Steel | Percentage of C | Mn | P | S | Si | Ni | Cr | Mo | Other |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Group O—Plain Carbon Steel | | | | | |
| O | 0.18 | 0.50 | 0.013 | 0.027 | 0.16 | .... | .... | .... | .... |
| | | | | Group A—C-Mo Steels | | | | | |
| A1 | 0.15 | 0.46 | 0.006 | 0.023 | 0.14 | .... | .... | 0.56 | .... |
| A2 | 0.16 | 0.43 | 0.015 | 0.013 | 0.16 | .... | .... | 1.10 | .... |
| A3 | 0.21 | 0.38 | 0.017 | 0.025 | 0.03 | .... | .... | 1.36 | .... |
| A4 | 0.13 | 0.33 | 0.014 | 0.022 | 0.01 | .... | .... | 1.95 | .... |
| A5 | 0.21 | 0.86 | 0.016 | 0.026 | 0.13 | .... | .... | 0.58 | .... |
| | | | | Group B—1-3 Cr-Mo Steels | | | | | |
| B1 | 0.12 | 0.47 | 0.008 | 0.007 | 0.22 | .... | 2.06 | 0.50 | .... |
| B2* | 0.10 | 0.34 | 0.012 | 0.007 | 0.12 | .... | 2.26 | 1.06 | .... |
| B3 | 0.14 | 0.43 | 0.011 | 0.008 | 0.84 | .... | 1.25 | 0.54 | .... |
| B4 | 0.17 | 0.52 | 0.012 | 0.014 | 0.57 | .... | 1.78 | 0.78 | .... |
| B5 | 0.12 | 0.48 | 0.010 | 0.011 | 1.57 | .... | 3.26 | 0.54 | .... |
| B6 | 0.08 | 0.32 | 0.010 | 0.011 | 1.43 | .... | 3.02 | 0.54 | Al 0.56 |
| | | | | Group C—5 Cr-Mo Steels | | | | | |
| C1 | 0.13 | 0.36 | 0.017 | 0.007 | 0.44 | .... | 5.48 | 0.50 | .... |
| C2* | 0.13 | 0.56 | 0.008 | 0.017 | 0.38 | .... | 5.66 | 0.98 | .... |
| C3 | 0.13 | 0.26 | 0.011 | 0.010 | 1.57 | .... | 5.24 | 0.50 | .... |
| C4 | 0.07 | 0.28 | 0.010 | 0.017 | 1.28 | .... | 4.96 | 0.54 | Al 0.58 |
| C5* | 0.05 | 0.34 | 0.010 | 0.008 | 0.39 | .... | 5.20 | 0.58 | Ti 0.47 |
| C6* | 0.09 | 0.42 | 0.012 | 0.011 | 0.35 | .... | 5.00 | 0.55 | Cb 0.49 |
| C7 | 0.06 | 0.40 | 0.010 | 0.018 | 1.04 | .... | 4.86 | 0.54 | Ti 0.39 |
| C8* | 0.08 | 0.42 | 0.019 | 0.016 | 1.05 | .... | 5.46 | 0.54 | Cb 0.50 |
| | | | | Group D—8-27 Cr Steels | | | | | |
| D1* | 0.10 | 0.36 | 0.011 | 0.009 | 0.31 | .... | 8.04 | 1.04 | .... |
| D2* | 0.09 | 0.56 | ..... | ..... | 0.33 | .... | 8.15 | 0.91 | Cb 0.59 |
| D3* | 0.12 | 0.43 | 0.011 | 0.015 | 0.43 | .... | 9.47 | 1.04 | .... |
| D4 | 0.06 | 0.38 | 0.008 | 0.004 | 0.36 | .... | 11.86 | 0.47 | .... |
| D5 | .... | .... | ..... | ..... | .... | .... | 27. | .... | .... |
| | | | | Group E—18 Cr-8 Ni Steels | | | | | |
| E1* | 0.05 | 0.28 | ..... | ..... | 0.43 | 9.85 | 18.40 | .... | .... |
| E2* | 0.05 | 0.52 | 0.017 | 0.010 | 0.39 | 10.90 | 17.50 | .... | Ti 0.44 |
| E3* | 0.07 | 1.51 | ..... | ..... | 0.32 | 11.12 | 18.10 | .... | Cb 0.82 |

*Steels for which creep data are presented in this report.

The creep tests were carried out on steels from Groups B, C, D, and E at 1000 and 1100 degrees Fahr. Creep tests have previously been published (1), (3) on steels in Group A at 1000 and 1100 degrees Fahr.; the tests now under way on steels from Group O will be reported at a later date. The oxidation tests were made at 1100, 1400, and 1700 degrees Fahr. (595, 760, 925 degrees Cent.).

### *Heat Treatment*

The heat treatments employed for the specimens subjected to creep test are shown in Table II. The ferritic Cr-Mo steels were furnace-cooled, the austenitic 18 Cr-8 Ni steel water-quenched, and the modified austenitic 18 Cr-8 Ni steels air-cooled. In certain cases, these treatments were followed by tempering or stabilizing. All specimens subjected to oxidation test were heated at 1650 degrees

**Table II**
**Heat Treatment of Creep Specimens**

| Steel | Designation of Specimen | Heat Treatment Schedule: Temp., ° F. | Time, Hrs. | Mode of Cooling | Temp., ° F. | Time, Hrs. | Mode of Cooling | Symbol |
|---|---|---|---|---|---|---|---|---|
| Group B | | | | | | | | |
| B2 | c, d | 1650 | 0.5 | Furnace | .... | .. | | FC |
| B2 | e, f | 1650 | 1 | Air | 1380 | 4 | Furnace | AC–FC |
| Group C | | | | | | | | |
| C2 | c, d | 1650 | 0.5 | Furnace | .... | .. | | FC |
| C2 | e, f | 1650 | 0.5 | Air | 1380 | 4 | Air | AC–AC |
| C5 | c, d | 1850 | 0.5 | Furnace | .... | .. | | FC |
| C6 | e, f | 1850 | 0.5 | Furnace | .... | .. | | FC |
| C8 | a, d | 1750 | 1 | Air | 1380 | 4 | Furnace | AC–FC |
| Group D | | | | | | | | |
| D1 | a, b | 1700 | 1 | Furnace (50° F. per hr.) | .... | .. | | FC |
| D2 | a, b | 1700 | 1 | Furnace (50° F. per hr.) | .... | .. | | FC |
| D3 | a, b | 1700 | 1 | Furnace (50° F. per hr.) | .... | .. | | FC |
| Group E | | | | | | | | |
| E1 | a, b | 1900 | 1 | Water | .... | .. | | WQ |
| E2 | a, b | 1900 | 1 | Air | .... | .. | | AC |
| E2 | c, d | 1900 | 1 | Air | 1600 | 2 | Air | AC–AC |
| E3 | a, b | 1900 | 1 | Air | .... | .. | | AC |
| E3 | c, d | 1900 | 1 | Air | 1600 | 2 | Air | AC–AC |

**Table III**
**Creep Test Data**

| Steel | Designation of Specimen | Nominal Composition | Heat Treatment (Degrees Fahr.) | Creep Test Temperature Degrees Fahr. | Creep Stress psi. | Duration of Creep Test Hours |
|---|---|---|---|---|---|---|
| B2 | a† | 2.25 Cr–1 Mo | 1650 AC, 1380 FC | 1000 | 15,000 | 3000 |
| B2 | b† | 2.25 Cr–1 Mo | 1650 AC, 1380 FC | 1000 | 10,000 | 3000 |
| B2 | c | 2.25 Cr–1 Mo | 1650 FC | 1000 | 15,000 | 3000 |
| B2 | d | 2.25 Cr–1 Mo | 1650 FC | 1000 | 10,000 | 3000 |
| B2 | e | 2.25 Cr–1 Mo | 1650 AC, 1380 FC | 1100 | 8,000 | 3000 |
| B2 | f | 2.25 Cr–1 Mo | 1650 AC, 1380 FC | 1100 | 5,000 | 3000 |
| C2 | a† | 5 Cr–1 Mo | 1650 AC, 1380 AC | 1000 | 15,000 | 1000 |
| C2 | b† | 5 Cr–1 Mo | 1650 AC, 1380 AC | 1000 | 10,000 | 2200 |
| C2 | c | 5 Cr–1 Mo | 1650 FC | 1000 | 15,000 | 500 |
| C2 | d | 5 Cr–1 Mo | 1650 FC | 1000 | 10,000 | 3000 |
| C2 | e | 5 Cr–1 Mo | 1650 AC, 1380 FC | 1100 | 8,000 | 1000 |
| C2 | f | 5 Cr–1 Mo | 1650 AC, 1380 FC | 1100 | 5,000 | 3000 |
| C5 | a† | 5 Cr–Mo–Ti | 1380 AC | 1000 | 15,000 | 1500 |
| C5 | b† | 5 Cr–Mo–Ti | 1380 AC | 1000 | 10,000 | 2200 |
| C5 | c | 5 Cr–Mo–Ti | 1850 FC | 1000 | 15,000 | 2000 |
| C5 | d | 5 Cr–Mo–Ti | 1850 FC | 1000 | 10,000 | 3000 |
| C6 | a† | 5 Cr–Mo–Cb | 1380 AC | 1000 | 15,000 | 2000 |
| C6 | c† | 5 Cr–Mo–Cb | 1380 AC | 1000 | 20,000 | 1500 |
| C6 | d† | 5 Cr–Mo–Cb | 1650 FC | 1000 | 15,000 | 900 |
| C6 | e | 5 Cr–Mo–Cb | 1850 FC | 1000 | 15,000 | 500 |
| C6 | f | 5 Cr–Mo–Cb | 1850 FC | 1000 | 10,000 | 3000 |
| C8 | a | 5 Cr–Mo–Cb–Si | 1750 AC, 1380 FC | 1000 | 15,000 | 1000 |
| C8 | b | 5 Cr–Mo–Cb–Si | 1750 AC, 1380 FC | 1000 | 10,000 | 3000 |
| D1 | a | 8 Cr–Mo | 1700 FC | 1100 | 4,000 | 3000 |
| D1 | b | 8 Cr–Mo | 1700 FC | 1100 | 6,000 | 3000 |
| D2 | a | 8 Cr–Mo–Cb | 1700 FC | 1100 | 4,000 | 3000 |
| D2 | b | 8 Cr–Mo–Cb | 1700 FC | 1100 | 6,000 | 3000 |
| D3 | a | 9 Cr–Mo | 1700 FC | 1100 | 4,000 | 3000 |
| D3 | b | 9 Cr–Mo | 1700 FC | 1100 | 6,000 | 3000 |
| E1 | a | 18–8 | 1900 WQ | 1100 | 13,000 | 3000 |
| E1 | b | 18–8 | 1900 WQ | 1100 | 15,000 | 3000 |
| E2 | a | 18–8 Ti | 1900 AC | 1100 | 13,000 | 3000 |
| E2 | b | 18–8 Ti | 1900 AC | 1100 | 15,000 | 3000 |
| E2 | c | 18–8 Ti | 1900 AC, 1600 AC | 1100 | 13,000 | 3000 |
| E2 | d | 18–8 Ti | 1900 AC, 1600 AC | 1100 | 10,000 | 3000 |
| E3 | a | 18–8 Cb | 1900 AC | 1100 | 19,000 | 3000 |
| E3 | b | 18–8 Cb | 1900 AC | 1100 | 25,000 | 3000 |
| E3 | c | 18–8 Cb | 1900 AC, 1600 AC | 1100 | 19,000 | 3000 |
| E3 | d | 18–8 Cb | 1900 AC, 1600 AC | 1100 | 15,000 | 3000 |

†Data from previous investigation (3).

Fahr. (900 degrees Cent.) and furnace-cooled prior to machining and testing.

### *Results of Creep Tests*

The new creep data, all from tests of 3000 hours' duration, are shown in Table III. For convenience of comparison, data from the previous investigation (3), and the creep strength determined by other investigators, are also presented.

**Table III (Continued)**
**Creep Test Data**

| Average Creep Rate During Last 1000 Hrs. Millionth in./in./hr. | Modified (2/3 size) Charpy Impact Strength Before Creep Test Ft.Lbs. | Modified (2/3 size) Charpy Impact Strength After Creep Test Ft.Lbs. | Brinell Hardness Before Creep Test | Brinell Hardness After Creep Test | Amount of Change of Microstructure During Creep | Stress for Creep Rate of 1 Millionth in./in./hr. Kearny | Stress for Creep Rate of 1 Millionth in./in./hr. Other Laboratories |
|---|---|---|---|---|---|---|---|
| 1.47 | 46 | 44 | 159 | 167 | None | 13,300 | |
| 0.54 | 46 | 42.5 | 159 | 163 | .... | ... | |
| 7.45 | 39 | 44 | 133 | 136 | Slight | 12,100 | {16,350 (B & W) |
| 0.24 | 39 | 45 | 133 | 136 | .... | ... | {11,000 (Timken) |
| 3.63 | .. | .. | ... | ... | .... | 5,700 | { 9,200 (B & W) |
| 0.66 | 46 | 43 | 159 | 136 | Moderate | ... | { 7,400 (Timken) |
| 7.9 | 39 | 33 | 202 | 174 | None | 10,800 | |
| 0.72 | 39 | 35 | 202 | 212 | .... | ... | |
| 39.8 | 29.5 | 29.5 | 140 | 138 | None | 8,400 | 10,000 (Climax) |
| 2.42 | 29.5 | 26 | 140 | 138 | .... | ... | |
| 17.5 | 39 | 30.5 | 181 | 158 | Slight | 4,300 | 4,900 (Timken) |
| 1.73 | 39 | 34 | 182 | 163 | .... | ... | |
| 32.3 | 52 | 44 | 149 | 134 | Slight | 11,500 | {13,000 (B & W) |
| 0.2 | 52 | 43 | 149 | 126 | .... | ... | {13,250 (UCC) |
| 79.3 | 49 | 48 | 112 | 127 | .... | 11,700 | 13,000 (B & W) |
| 0.14 | 49 | 47 | 112 | 123 | None | ... | |
| 0.28 | 49 | 36 | 169 | 156 | Slight | 16,400 | 16,500 (UCC) |
| 12.8 | 49 | 47.5 | 169 | 163 | .... | ... | |
| 41.7 | 46.5 | 38 | 140 | 140 | .... | ... | |
| 89.2 | 43.5 | 35 | 127 | 131 | None | 9,500 | |
| 1.0 | 43.5 | 38 | 127 | 124 | .... | ... | |
| 35.0 | 42 | 42 | 152 | 154 | .... | 10,900 | |
| 0.48 | 42 | 33 | 152 | 147 | None | ... | |
| 0.20 | 23 | 28 | 145 | 141 | None | 5,600 | { 6,950 (B & W) |
| 1.53 | 23 | 24.5 | 145 | 139 | None | ... | { 6,200 (Timken) |
| 0.05 | 41 | 22.5 | 141 | 138 | None | 8,000 | 7,000 (UCC) |
| 0.22 | 41 | 20 | 141 | 139 | None | ... | |
| 0.22 | 23 | 22 | 144 | 143 | None | 5,200 | { 6,950 (B & W) |
| 3.47 | 23 | 23.5 | 144 | 146 | None | ... | { 6,200 (Timken) |
| 0.79 | 56.5 | 42 | 153 | 155 | Moderate | 13,500 | {11,500 (B & W) |
| 2.18 | .. | .. | ... | ... | .... | ... | {13,200 (Timken) |
| | | | | | | | {13,500 (UCC) |
| 0.62 | 53 | 41 | 143 | 144 | Slight | 13,600 | |
| 2.95 | .. | .. | ... | ... | .... | ... | |
| 1.66 | 50 | 43.5 | 141 | 147 | None | 12,600 | |
| 0.12 | .. | .. | ... | ... | .... | ... | |
| 0.29 | 42.5 | 34 | 165 | 172 | Slight | 22,200 | 23,500 (UCC) |
| 3.68 | .. | .. | ... | ... | .... | ... | |
| 1.57 | 42.5 | 33 | 158 | 176 | Slight | 18,000 | 20,750 (UCC) |
| 0.33 | .. | .. | ... | ... | .... | ... | |

*Group B, 1-3 per cent Cr-Mo Steels*—The stress for a creep rate of 1 millionth in/in/hr (hereafter referred to as the "creep strength") of steel B2 (2.25 Cr-1 Mo) at 1000 degrees Fahr. is higher in the air-cooled and tempered than in the furnace-cooled condition (13,300 as compared to 12,100 psi). At 1100 degrees Fahr., its creep strength in the air-cooled and tempered condition is 5700 psi.

*Group C, 5 per cent Cr-Mo Steels*—At 1000 degrees Fahr., the

creep strength of steel C2 (5 Cr-1 Mo) is higher in the air-cooled and tempered than in the furnace-cooled condition (10,800 as compared to 8400 psi); at 1100 degrees Fahr., in the air-cooled and tempered condition it is 4300 psi.

At 1000 degrees Fahr., the creep strength of steel C5 (5 Cr-Mo-Ti) is about the same in the hot-rolled and tempered as in the furnace-cooled condition (11,500 as compared to 11,700 psi).

At 1000 degrees Fahr., the creep strength of steel C6 (5 Cr-Mo-Cb) is higher in the hot-rolled and tempered than in the furnace-cooled condition (16,400 as compared to 9500 psi). This agrees with the results of the previous investigation (3) in which it was found that specimen C6d, furnace-cooled from 1650 degrees Fahr. (900 degrees Cent.), had a creep rate of 41.7 millionths in/in/hr under a stress of 15,000 psi at 1000 degrees Fahr., while specimen C6a, in the hot-rolled and tempered condition, had a creep rate of only 0.28 millionths in/in/hr under the same test conditions. It is believed that the high strength of the hot-rolled and tempered steel is the result of a fortuitous choice of conditioning treatment and tempering time, resulting in a beneficial distribution of a precipitate

**Table IV**
**Transformation Temperatures of 8 and 9 Cr-Mo Steels**

| Steel | Nominal Composition | Approximate $A_1$ Temperature Degrees Fahr. | Approximate $A_3$ Temperature Degrees Fahr. |
|---|---|---|---|
| D1 | 8 Cr–1 Mo | 1475 | 1600 |
| D2 | 8 Cr–1 Mo–Cb | 1450 | 1650 |
| D3 | 9 Cr–1 Mo | 1500 | 1600 |

throughout the structure. In the furnace-cooled condition, this steel has about the same creep strength as the same material without columbium (steel C1, 5 Cr-1/2 Mo). Addition of silicon to air-cooled and tempered 5 Cr-Mo-Cb steel decreases its creep strength from 16,400 (C6) to 10,900 (C8) psi at 1000 degrees Fahr.

*Group D, 8-9 per cent Cr-Mo Steels*—Since these steels had not been previously investigated, their $A_1$ and $A_3$ temperatures were determined within ±25 degrees Fahr. (Table IV). It was found that the carbides in these steels dissolved quite slowly in austenite, and it was necessary to hold the creep specimens for one hour at 1700 degrees Fahr. in order to obtain solution of the carbides; the specimens were then furnace-cooled at a controlled rate of about 50 degrees Fahr. per hour in order to avoid air hardening†. Owing

†The hardness of one-inch sections of 8 Cr-1 Mo, 8 Cr-1 Mo-Cb, and 9 Cr-1 Mo steels air-cooled from 1700 degrees Fahr. was 408, 336, and 436 VPN respectively.

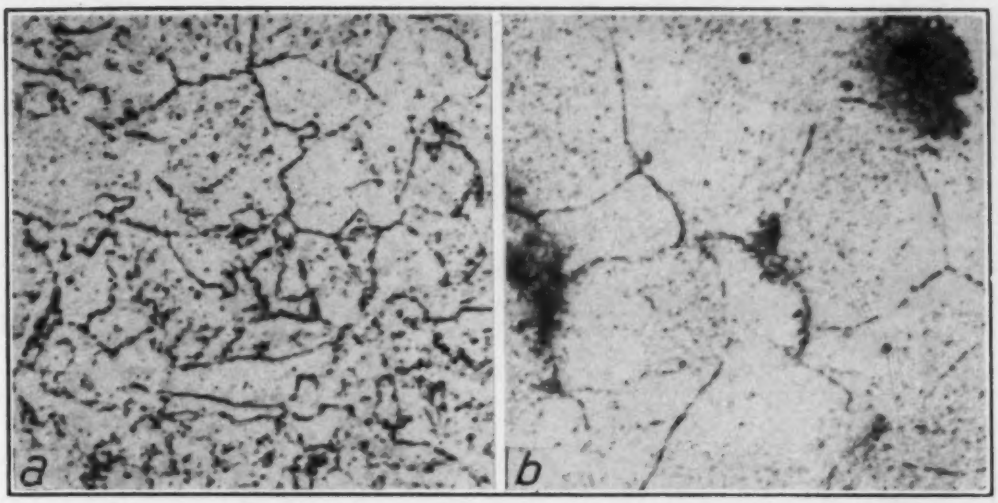


Fig. 1—Microstructure of Steel B2 (2.25 Chromium-1.00 Molybdenum) Before Creep Testing. Picral-Nital Etch. × 1000. (a)—1650 Degrees Fahr., FC, 133 VPN. (b)—1650 Degrees Fahr., AC; 1380 Degrees Fahr., FC, 159 VPN.

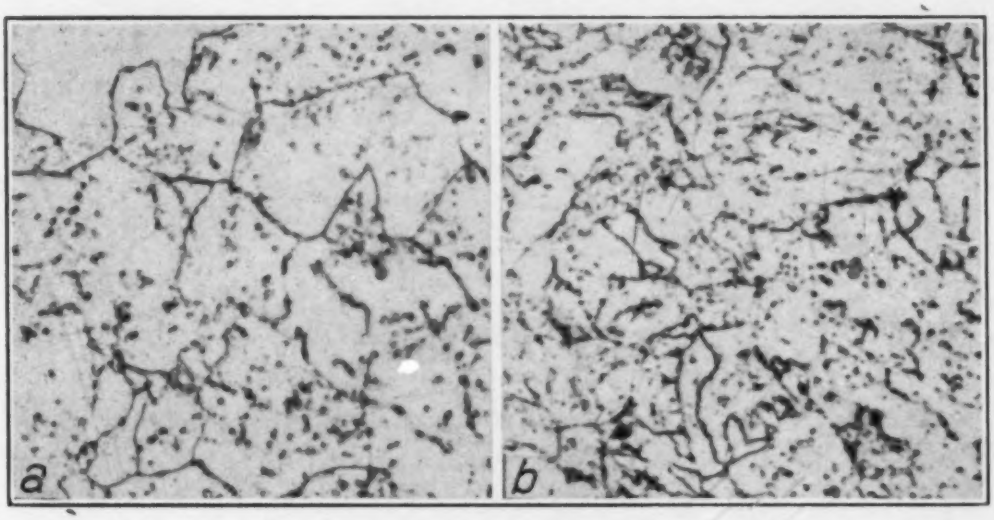


Fig. 2—Microstructure of Steel C2 (5.00 Chromium-1.00 Molybdenum) Before Creep Testing. Picral-Nital Etch. × 1000. (a)—1650 Degrees Fahr., FC, 140 VPN. (b)—1650 Degrees Fahr., AC; 1380 Degrees Fahr., AC, 181 VPN.

to the high alloy content, the transformation rate of these steels is so slow, that some martensite forms when the steel is cooled at a rate of 200 degrees Fahr. per hour but none at 100 degrees Fahr. per hour.

At 1100 degrees Fahr. the creep strength of the furnace-cooled 8 Cr-1 Mo steel (D1) was 5600 psi. Increase of chromium content to 9 per cent (steel D3) caused a slight decrease in creep strength (to 5200 psi.). Addition of columbium to the 8 Cr-1 Mo steel (D2) increased the creep strength to 8000 psi.

*Group E, 18 Cr-8 Ni Steels*—At 1100 degrees Fahr., the creep strength of water-quenched 18-8 (E1) and air-cooled 18-8 Ti (E2) is about the same (13,500 and 13,600 psi). Stabilization of the air-cooled 18-8 Ti (E2) by heating for 2 hours at 1600 degrees Fahr. reduces its creep strength at 1100 degrees Fahr. from 13,600 to 11,600 psi. The creep strength at 1100 degrees Fahr. of 18-8 Cb (E3) in the air-cooled condition (22,200 psi) is considerably above that of the other 18-8 steels; this high value is reduced by the stabil-

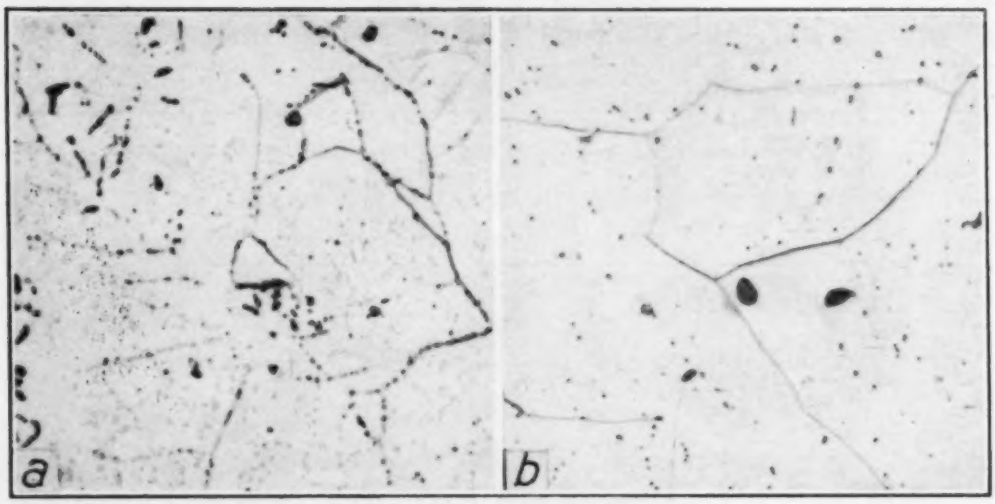


Fig. 3—Microstructure of Steel C5 (5.00 Chromium-Molybdenum-Titanium) Before Creep Testing. Picral-Nital Etch. × 1000. (a)—1380 Degrees Fahr., AC, 149 VPN. (b)—1850 Degrees Fahr., FC, 112 VPN.

ization treatment to 18,000 psi, still above that of the other 18-8 steels. Confirmatory data are now available on three other heats of 18-8 Cb, indicating that high strength is a general characteristic of this type of material.

Summarizing, it appears from Table III that the creep strength of the Cr-Mo steels is higher in the air-cooled and tempered than in the furnace-cooled condition.* The creep strength of 18-8 Ti and 18-8 Cb was found to be higher at 1100 degrees Fahr. in the air-cooled than in the air-cooled and stabilized condition. The present results are in fair agreement with those of previous investigators except for steel B2 (2.25 Cr-1 Mo), where the present values are somewhat lower than theirs.

*However, it was previously (3) found that the creep strength of steel C1 (5 Cr-1 Mo) at 1000 degrees Fahr. was higher in the furnace-cooled than in the air-cooled and tempered condition.

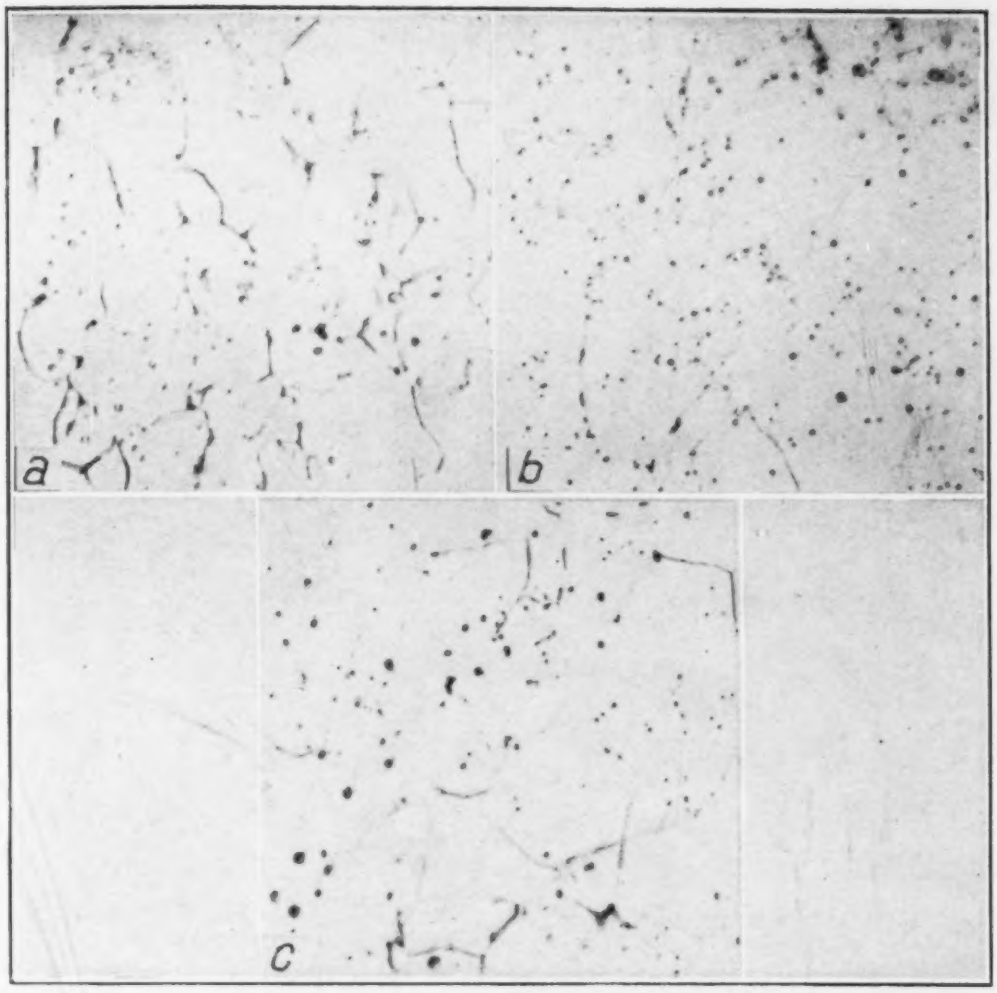


Fig. 4—Microstructure of Steel C6 (5.00 Chromium-Molybdenum-Columbium) Before Creep Testing. Picral-Nital Etch. × 1000. (a)—1300 Degrees Fahr., AC, 169 VPN. (b)—1650 Degrees Fahr., FC, 140 VPN. (c)—1850 Degrees Fahr., FC, 127 VPN.

### *Hardness*

No significant change in the hardness of the furnace-cooled Cr-Mo steels occurred during creep test at 1000 or 1100 degrees Fahr. (Table III), but there was a small decrease in hardness of some of the air-cooled and tempered materials. A slight increase in hardness was noted in the 18-8 materials at 1100 degrees Fahr., particularly in the 18-8 Cb steel (E3).

### *Impact Strength*

The impact strength of the Cr-Mo and 18 Cr-8 Ni steels decreased slightly during creep test, except in the case of furnace-cooled

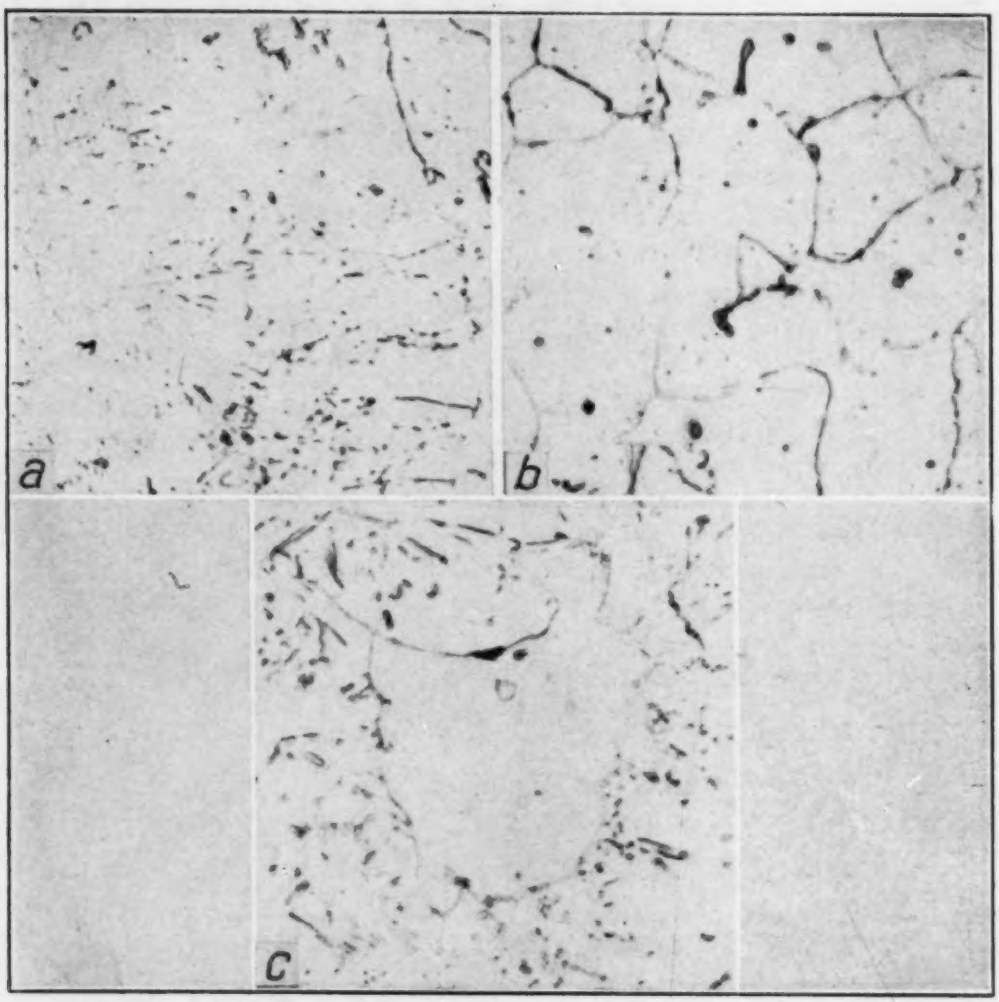


Fig. 5—Microstructure of Steels D1, D2 and D3 Before Creep Testing. Furnace-Cooled at 50 Degrees Fahr. Per Hour from 1700 Degrees Fahr. Marble's Reagent. × 1000. (a)—Steel D1 (8.00 Chromium-1.00 Molybdenum) 145 VPN. (b)—Steel D2 (8.00 Chromium-Molybdenum-Columbium) 141 VPN. (c)—Steel D3 (9.00 Chromium-1.00 Molybdenum) 144 VPN.

steel B2 (2.25 Cr-1 Mo) at 1000 degrees Fahr., where a small increase occurred (Table III).

### *Microstructure*

The "before creep" microstructure of the Cr-Mo steels of Groups B, C, and D consists of carbide particles of varying degrees of dispersion in a ferrite matrix (Figs. 1-6). Some of the Cr-Mo steels of Groups B and C showed no change of microstructure during creep test at 1000 degrees Fahr., while others showed a slight change; during creep test at 1100 degrees Fahr., a slight to moderate change was encountered. These changes were in the nature of

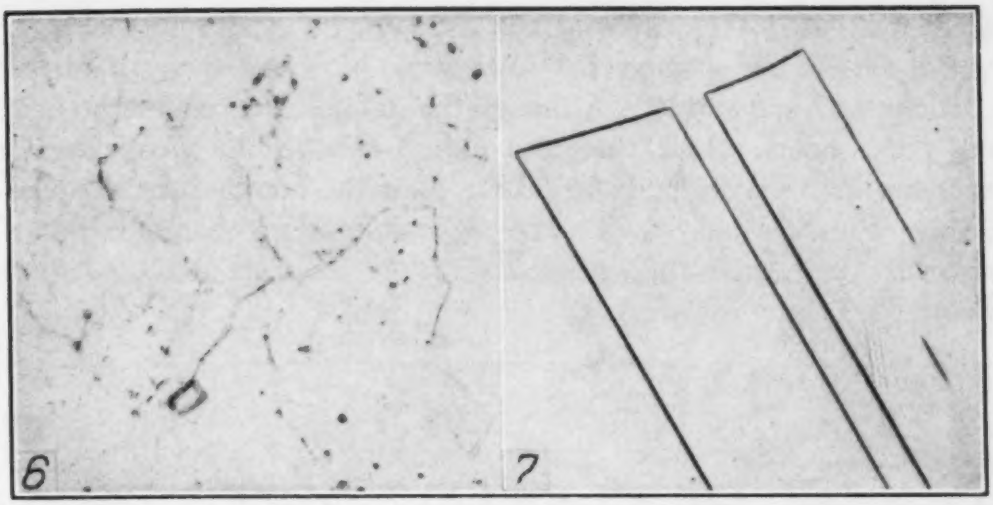


Fig. 6—Microstructure of Steel C8 (5.00 Chromium-Molybdenum-Columbium-Silicon) Before Creep Testing. 1750 Degrees Fahr., AC; 1380 Degrees Fahr., FC. Picral-Nital Etch. 152 VPN. × 1000.

Fig. 7—Microstructure of Steel E1 (18-8) Before Creep Testing. 1900 Degrees Fahr., WQ: Glyceregia Etch. 153 VPN. × 1000.

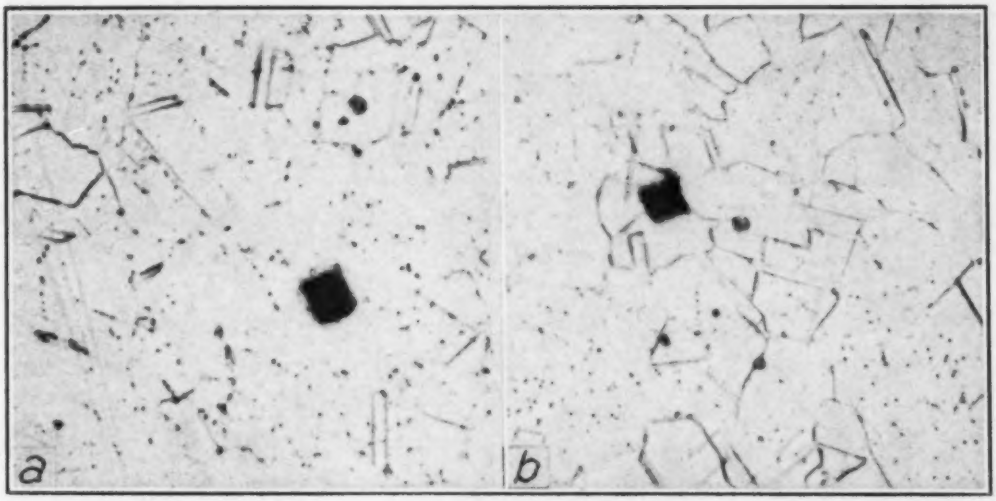


Fig. 8—Microstructure of Steel E2 (18-8 Titanium) Before Creep Testing. Glyceregia Etch. × 1000. (a)—1900 Degrees Fahr., AC, 141 VPN. (b)—1900 Degrees Fahr., AC; 1600 Degrees Fahr., AC.

spheroidization or agglomeration of the carbide particles. Neither furnace cooling nor air cooling and tempering showed any superiority over one another in regard to producing a more stable microstructure either at 1000 or 1100 degrees Fahr. There was no change in microstructure of the 8 and 9 Cr-Mo steels of Group D during creep test.

Steel E1 (18 Cr-8 Ni), Fig. 7, shows quite large twinned austenite grains and a rather clear background. Pronounced grain boundary precipitation of carbides occurred in this material during

creep test at 1100 degrees Fahr. Steels E2 (18-8 Ti) and E3 (18-8 Cb) show a somewhat finer grain size and many dispersed particles (Figs. 8 and 9). Although the stabilization treatment (heating for 2 hours at 1600 degrees Fahr.) resulted in a considerable decrease in creep strength, it did not alter the microstructure appreciably (Figs. 8a and 8b, 9a and 9b). Little or no change in microstructure occurred in these materials during creep test at 1100 degrees Fahr. (595 degrees Cent.).

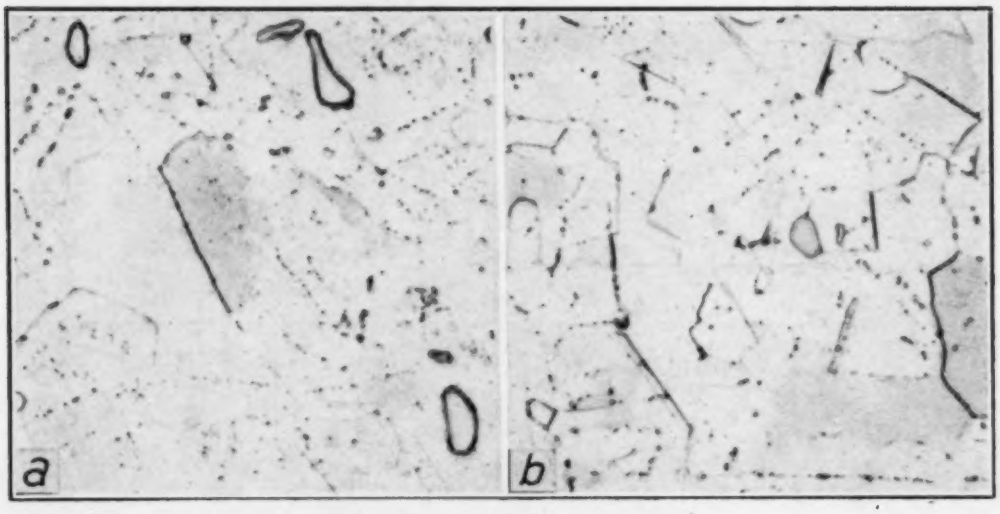


Fig. 9—Microstructure of Steel E3 (18-8 Columbium) Before Creep Testing. Glyceregia Etch. × 1000. (a)—1900 Degrees Fahr., AC, 165 VPN. (b)—1900 Degrees Fahr., AC; 1600 Degrees Fahr., AC. 158 VPN.

The effect of time at temperature on the microstructure of the 17 low-alloy steels tested in creep at 1000 degrees Fahr. was summarized in the paper by Miller, Benz, and Unverzagt (3). In order to extend this study of the effect of time at temperature on microstructure, the steels which showed no structural change during creep at 1000 degrees Fahr. were heated for 3000 hours at 1100 degrees Fahr., and those which showed moderate or marked change at 1000 degrees Fahr. were heated for 3000 hours at 900 degrees Fahr.* It was assumed that those steels showing change at 1000 degrees Fahr. would do so at a higher temperature, and that those which remain unchanged at 1000 degrees Fahr. would do likewise at a lower temperature. The results of these tempering tests have been combined with those of the present and previous creep tests, and the relative

*Half-disk specimens, ½ inch thick and 1 inch in diameter, were heated in periodically deoxidized lead baths held at the appropriate temperature. Although the specimens were under no stress, the structural changes were believed to be comparable with those encountered in creep tests since stresses of the magnitude of those producing a creep rate of 1.0 or 0.1 millionth in /in/hr have not been found to accelerate structural change.

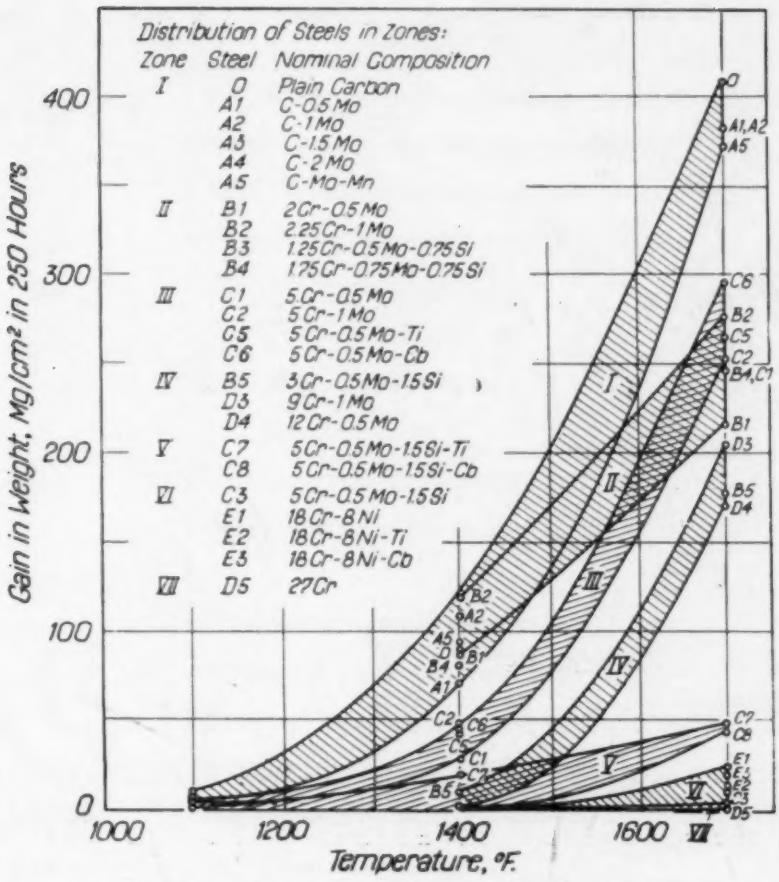


Fig. 10—Amount of Oxidation (Scaling) in 250 Hours.

change in microstructure occurring in 3000 hours at the various temperatures is summarized in Table V. The first trace of spheroidization of air-cooled (pearlitic) C-0.5 Mo steel (A1) was found after 3000 hours at 900 degrees Fahr., but in the tempered material, and in the steels containing a larger amount of molybdenum, the first change occurred at 1000 degrees Fahr. Tempering of the air-cooled C-Mo steels increased their structural stability at 1000 degrees Fahr. As previously noted (3), addition of chromium increased the stability of the carbides, and little or no change occurred in the Cr-Mo steels at 1000 or 1100 degrees Fahr.

### *Amount of Oxidation*

The amount of oxidation (scaling) of the steels was determined in 1000-hour tests at 1100, 1400 and 1700 degrees Fahr. by periodic measurement of the weight gain of oxygen. A novel apparatus has been employed (2), which consists essentially of an annular furnace

**Table V**

**Relative Change of Microstructure* of Alloys During 3000 Hours at 900 and 1100 Degrees Fahr.**

| Steel | Designation of Specimen | Nominal Composition | Heat Treatment | Change of Structure in 3000 Hours at 900 ° F. | 1000 ° F. | 1100 ° F. |
|---|---|---|---|---|---|---|
| A1 | a, b | C–0.5 Mo | 1650 AC | I | III | III |
| A1 | c, d | C–0.5 Mo | 1650 AC, 1300 AC | O | II | III |
| A2 | a, b | C–1 Mo | 1650 AC | O | III | .. |
| A2 | c, d | C–1 Mo | 1650 AC, 1300 AC | O | II | .. |
| A3 | a, b | C–1.5 Mo | 1650 AC | O | III | .. |
| A3 | c, d | C–1.5 Mo | 1650 AC, 1300 AC | O | II | .. |
| A4 | a, b | C–2 Mo | 1650 AC | O | III | .. |
| A4 | c, d | C–2 Mo | 1650 AC, 1300 AC | .. | II | .. |
| A5 | a, b | C–Mo–Mn | 1650 AC, 1300 AC | O | II | .. |
| B1 | a, b | 2 Cr–0.5 Mo | 1650 AC, 1380 FC | .. | I | .. |
| B2 | a, b | 2.25 Cr–1 Mo | 1650 AC, 1380 FC | .. | O | II |
| B2 | c, d | 2.25 Cr–1 Mo | 1650 FC | .. | I | .. |
| B3 | b, c, d | 1.2 Cr–0.5 Mo–0.7 Si | 1650 AC 1380 FC | .. | O | II |
| B4 | a, b | 1.7 Cr–0.7 Mo–0.7 Si | 1750 AC 1375 FC | .. | I | .. |
| B5 | a, b, c | 3 Cr–0.5 Mo–1.5 Si | 1600 FC | .. | O | O |
| B6 | a, b, c | 3 Cr–Mo–Si–Al | 1550 AC | .. | O | O |
| C1 | a, b | 5 Cr–0.5 Mo | 1600 FC | .. | O | O |
| C1 | c, d, e | 5 Cr–0.5 Mo | 1600 AC, 1380 AC | .. | O | I |
| C2 | a, b, e, f | 5 Cr–1 Mo | 1650 AC, 1380 AC | .. | O | I |
| C2 | c, d | 5 Cr–1 Mo | 1650 FC | .. | O | .. |
| C3 | a, b, c | 5 Cr–0.5 Mo–1.5 Si | 1600 FC | .. | O | O |
| C4 | a, b, c | 5 Cr–Mo–Si–Al | 1550 AC | .. | O | O |
| C5 | a, b | 5 Cr–Mo–Ti | 1380 AC | .. | I | .. |
| C5 | c, d | 5 Cr–Mo–Ti | 1850 AC | .. | O | .. |
| C6 | a, c | 5 Cr–Mo–Cb | 1380 AC | .. | I | .. |
| C6 | e, f | 5 Cr–Mo–Cb | 1850 AC | .. | O | .. |
| C8 | a, b | 5 Cr–Mo–Si–Cb | 1750 AC, 1380 FC | .. | O | .. |
| D1 | a, b | 8 Cr–1 Mo | 1700 FC | .. | O | O |
| D2 | a, b | 8 Cr–1 Mo–Cb | 1700 FC | .. | O | O |
| D3 | a, b | 9 Cr–1 Mo | 1700 FC | .. | O | O |
| E1 | a, b | 18–8 | 1900 WQ | .. | .. | II |
| E2 | a, b | 18–8 Ti | 1900 AC | .. | .. | I |
| E2 | c, d | 18–8 Ti | 1900 AC, 1600 AC | .. | .. | O |
| E3 | a, b | 18–8 Cb | 1900 AC | .. | .. | I |
| E3 | c, d | 18–8 Cb | 1900 AC, 1600 AC | .. | .. | I |

O —no change.
I —slight change.
II —moderate change.
III—marked change.

*It may be assumed that steels showing a change of microstructure at 1000 degrees Fahr would do so at a higher temperature, and that steels which remained unchanged at 1000 or 1100 degrees Fahr. would do likewise at a lower temperature.

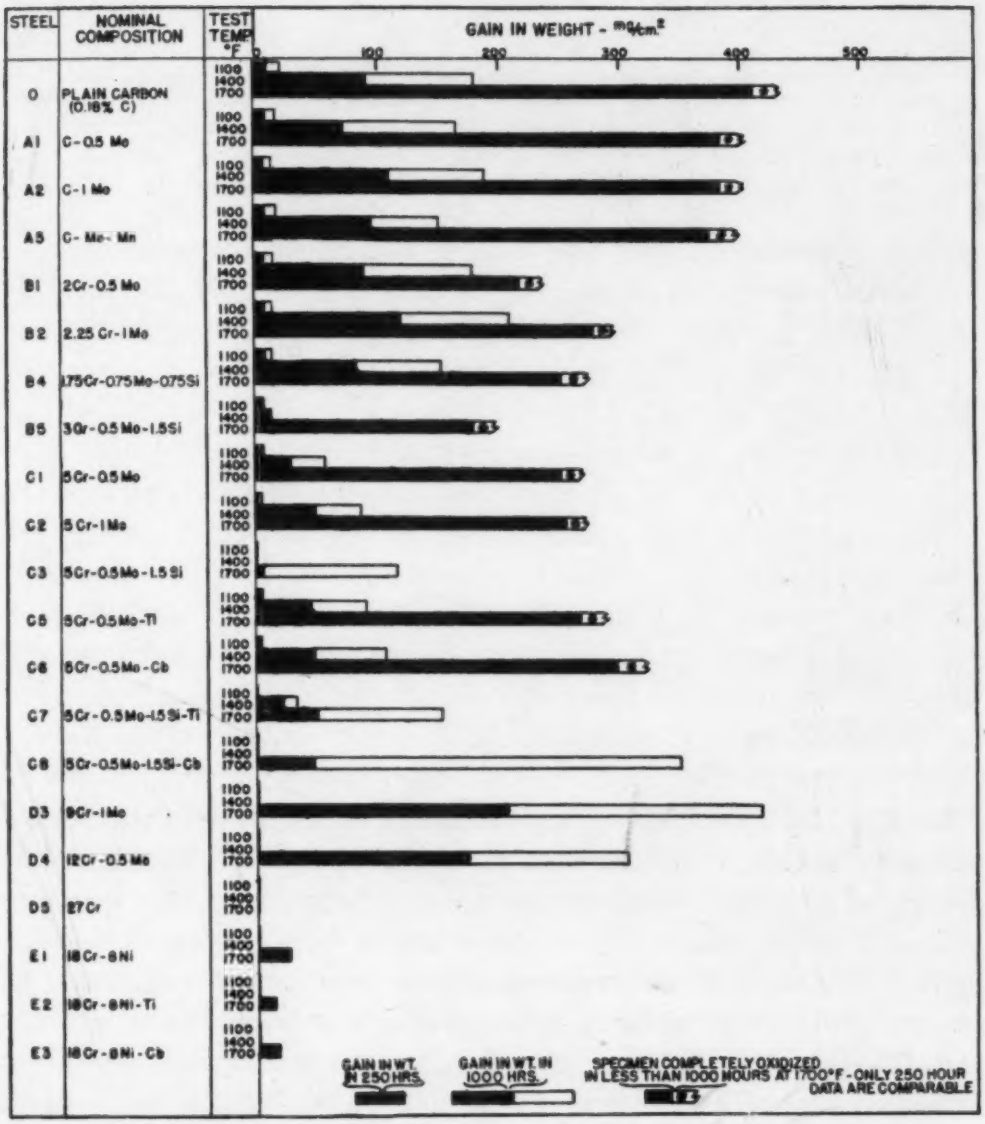


Fig. 11—Amount of Oxidation (Scaling) of Various Alloys in 250 and 1000 Hours at 1100, 1400, and 1700 Degrees Fahr.

in which 40 specimens are suspended by nichrome wires extending out of the top of the muffle or hood. The hood may be rotated continuously or intermittently, thus increasing the uniformity of temperature of the specimens and permitting each specimen to be brought under the extended pan of the analytical balance for weighing without removal of the specimen from the furnace.

The composition of the steels tested for amount of oxidation is shown in Table I. Of the three 8-9 Cr-Mo steels (D1, D2 and D3), only D3 (9 Cr-1 Mo) was tested for oxidation resistance, but it is believed that the oxidation resistance of 8 Cr-1 Mo (D1) and 8 Cr-

**Table VI**
**Results of Oxidation Tests**

| Steel | Nominal Composition | Gain in Weight, mg/cm², in 250 Hrs. at 1100 ° F. | 1400 ° F. | 1700 ° F. | Gain in Weight, mg/cm², in 1000 Hrs. at 1100 ° F. | 1400 ° F. | 1700 ° F. |
|---|---|---|---|---|---|---|---|
| O | Plain Carbon (0.18 C) | 8.8e | 92.1 | 413 | 20.6e | 182 | ... |
| A1 | C–0.5 Mo | 8.1 | 72.5 | 385 | 16.5 | 166 | ... |
| A2 | C–1 Mo | 7.0e | 111.3 | 385 | 13.0e | 190 | ... |
| A3 | C–1.5 Mo | 6.8 | .... | ... | 12.1 | ... | ... |
| A4 | C–2 Mo | 7.5 | .... | ... | 14.3 | ... | ... |
| A5 | C–Mo–Mn | 7.4 | 96.8 | 376 | 17.8 | 152 | ... |
| B1 | 2 Cr–0.5 Mo | 7.1 | 89.7 | 218 | 13.9 | 180 | ... |
| B2 | 2.25 Cr–1 Mo | 7.6 | 121.0 | 280 | 12.6 | 210 | ... |
| B3 | 1.25 Cr–0.5 Mo–0.75 Si | 8.1 | .... | ... | 13.9 | ... | ... |
| B4 | 1.75 Cr–0.75 Mo–0.75 Si | 8.0e | 82.6 | 252 | 13.0e | 153 | ... |
| B5 | 3 Cr–0.5 Mo–1.5 Si | 3.1 | 10.0 | 179 | 4.9 | 10.5 | ... |
| C1 | 5 Cr–0.5 Mo | 3.1 | 28.9 | 252 | 4.9 | 57.0 | ... |
| C2 | 5 Cr–1 Mo | 2.4 | 48.7 | 255 | 3.1 | 85.0 | ... |
| C3 | 5 Cr–0.5 Mo–1.5 Si | 0.5 | 0.2 | 5.2 | 0.1 | 0.3 | 117 |
| C5 | 5 Cr–0.5 Mo–Ti | 2.4 | 44.2 | 267 | 3.9 | 89.0 | ... |
| C6 | 5 Cr–0.5 Mo–Cb | 2.4 | 47.8 | 297 | 2.9 | 106.0 | ... |
| C7 | 5 Cr–0.5 Mo–1.5 Si–Ti | ... | 20.6 | 50.2 | ... | 33.0 | 153 |
| C8 | 5 Cr–0.5 Mo–1.5 Si–Cb | ... | 1.3 | 47.2 | ... | 0.7 | 350 |
| D3 | 9 Cr–1 Mo | ... | 0.3 | 207 | ... | 0.4 | 417 |
| D4 | 12 Cr–0.5 Mo | ... | 0.2 | 174 | ... | 0.3 | 307 |
| D5 | 27 Cr | ... | 0 | 1.2 | ... | 0.1 | 2.1 |
| E1 | 18 Cr–8 Ni | ... | 0.1 | 26.6 | ... | 0.2 | 27.0 |
| E2 | 18 Cr–8 Ni–Ti | ... | .... | 14.0 | ... | ... | 14.1* |
| E3 | 18 Cr–8 Ni-Cb | ... | .... | 17.7 | ... | ... | 17.7* |

e = estimate.
* = 450-hour test.

1 Mo-Cb (D2) would be quite similar. The material, in the form of one-inch rounds, was forged to plates ¼ inch thick, heated at 1650 degrees Fahr. and furnace-cooled and machined to flat specimens 1 x 2⅜ x ⅛ inches; the corners and edges were rounded to a $\frac{1}{16}$-inch radius, and the entire specimen was polished through 320 paper. A ⅛-inch hole was drilled through one end of the specimen and fitted with a tubular porcelain insulator, through which the nichrome supporting wire was threaded; this arrangement kept the wire separated from the surface of the specimen.

The results are listed in Table VI and plotted graphically in Figs. 10 and 11. At 1700 degrees Fahr. (925 degrees Cent.) some of the specimens were oxidized completely in a few hundred hours, and thus the weight of such specimens at 1000 hours is meaningless and is not reported. In order to compare all of the various alloys, the gain in weight in 250 hours is plotted against the temperature of test (Fig. 10). The alloys may be divided arbitrarily into seven zones, listed below in order of increasing oxidation resistance—the poorest being at the top of the list and the best at the bottom. It will be noted that these zones do not contain the same steels as the composition groups of Table I.

| Zone | Nominal Composition |
|---|---|
| I | Carbon and C-Mo Steels |
| II | 1 to 3 Cr-Mo Steels |
| III | 5 Cr-Mo Steels |
| IV | 3 Cr-Mo-Si and 9 to 12 Cr-Mo Steels |
| V | 5 Cr-Mo-Si (with Ti or Cb) Steels |
| VI | 5 Cr-Mo-Si and 18-8 Steels |
| VII | 27 Cr |

Another graphical presentation of the oxidation data is shown in Fig. 11. In this bar diagram, it is possible to show both the weight gain in 250 hours (black portion), and the weight gain in 1000 hours (the length of the black portion plus the length of the white portion). The advantage of this method of presentation of the data is that it gives an indication of the relative rate of scaling. For example, if the length of the black area is about equal to the length of the white area, the amount of oxidation in 250 hours is equal to that which occurs in the subsequent 750 hours. If little or none of the white area is visible, practically all of the oxidation occurs in the first 250 hours, and little or no oxidation takes place in the subsequent 750 hours. An example of this latter behavior is given by steel C3 (5 Cr-Mo-Si) at 1400 degrees Fahr.; the amount of oxidation in 250 hours was 0.2 mg/cm², while the total in 1000 hours was only 0.3 mg/cm². On the other hand, steel C3 behaves quite differently at 1700 degrees Fahr.; the weight gain in 250 hours at this temperature was 5.2 mg/cm² while in 1000 hours the weight gain was 117 mg/cm². Thus, if the test had been run for only 250 hours, this steel would have been rated as superior to steel E1 (18 Cr-8 Ni) in which the weight gain in 250 hours was 26.6 mg/cm². However, at the end of 1000 hours, the weight gain of the 18-8 steel was only 27.0 mg/cm², while the weight gain of steel C3 (5 Cr-Mo-Si) was 117 mg/cm². This rather high resistance to oxidation during the early part of the test at 1700 degrees Fahr. is characteristic of the high silicon Cr-Mo steels, and could be very misleading if the test were not run long enough to give an indication of long-time service behavior. With the exception of the Cr-Mo-Si steels at 1700 degrees Fahr., the general order of oxidation resistance at the end of 250 hours was found to be the same as that at the end of 1000 hours.

The following conclusions become evident from examination of Table VI and Figs. 10 and 11. At 1100 and 1400 degrees Fahr. the amount of oxidation of the steels in Groups O, A, and B (plain carbon, C-Mo and 1-3 per cent Cr-Mo) is of about the same order of magnitude, whether the results of the 250 or the 1000-hour tests

are considered. After 250 hours at 1700 degrees Fahr., less oxidation has occurred in the Cr-bearing steels than in those without chromium but the rate of oxidation is so rapid that the steels of Group O, A, and B are completely oxidized in 1000 hours. The addition of 5 per cent Cr decreases the amount of oxidation considerably. Increase of silicon from 0.50 to 0.75 per cent does not appear to improve the materials, but 1.5 per cent Si, added either to a 3 Cr-Mo or a 5 Cr-Mo steel, produces marked improvement. The addition of titanium or columbium to 5 Cr-Mo steel produces little change at 1100 degrees Fahr., but increases the amount of oxidation of 5 Cr-Mo and 5 Cr-Mo-Si steel at 1400 and 1700 degrees Fahr. Neither titanium nor columbium appears to have any definite advantage over one another, one being better at one temperature and another at a different temperature. Increase of chromium content from 9 to 12 to 27 per cent decreases the amount of oxidation, 27 Cr being the best material examined.

ACKNOWLEDGMENTS

The authors wish to acknowledge the assistance of Dr. G. V. Smith and Mr. P. A. Jennings in carrying out the tests, and the courtesy of the National Tube Company in supplying the materials.

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## DISCUSSION

**Written Discussion:** By George F. Comstock, metallurgist, The Titanium Alloy Manufacturing Co., Niagara Falls, N. Y.

We are fortunate in having this excellent report of the work on creep and oxidation-resistant steels that has been recently carried out by Mr. Miller and his associates. The inclusion in Table III of comparable results from other laboratories is especially commendable and adds greatly to the reference value of the paper. It would have been interesting to have a similar comparison of oxidation test data.

The authors apparently found it difficult to account for the superior creep resistance of the 5 per cent chromium-molybdenum-columbium steel C6 after tempering at 1380 degrees Fahr. (750 degrees Cent.) as compared with the similar steel containing titanium instead of columbium. The latter, however, had a titanium-carbon ratio of 9.4, while the columbium-carbon ratio of the former was only 5.4. The titanium steel was, therefore, fully stabilized against air hardening, while the columbium steel was not and did not come anywhere near the A.S.T.M. standard of at least 8 times as much columbium as carbon. Although no air hardening data are given here, it is obvious from past experience that the columbium in this steel was not sufficient to perform the function for which columbium, or titanium, is used in this kind of steel, and the creep data do not, therefore, apply to columbium steel properly stabilized against air hardening and meeting the A.S.T.M. specifications. Creep data on such steel would be very desirable to complete the authors' work.

Possibly the columbium content of steel C6 was intentionally restricted to improve its creep value, but if so the same procedure should have been adopted for titanium. The titanium-carbon ratio has been found in our laboratory to have an extremely important effect on the high-temperature strength properties of 5 per cent chromium-molybdenum-titanium steel as shown by stress-rupture tests. For instance two of these steels containing 0.08 per cent carbon were tested at 1200 degrees Fahr. (650 degrees Cent.) under stress of 8000 pounds per square inch, with the following results:

In the 1550 degrees Fahr. (845 degrees Cent.) annealed condition, the steel with titanium-carbon ratio of 6.1 failed after 242 hours, while the steel with a ratio of 3.8 did not fail in 2314 hours.

In the 1350 degrees Fahr. (730 degrees Cent.) tempered condition, the results were 630 hours with titanium-carbon ratio of 6.1, and over 2610 hours with the 3.8 ratio.

Other supporting data are also available to confirm this influence of the titanium-carbon ratio on stress-rupture values. Probably similar results would be obtained in creep testing, though as yet we have no definite data. Some creep tests of a 5 per cent chromium-molybdenum-titanium steel with a titanium-carbon ratio around 4 or 5 (or even as low as 3 to compare with the columbium steel C6) would be very desirable to complete the authors' work. It seems quite unfortunate to generalize regarding comparative creep properties of these various grades of steel from results obtained on only a single heat of each,

yet this seems to have been a fairly common practice of other investigators besides the authors.

The final statement of the authors that titanium increases the amount of oxidation of the 5 per cent chromium-molybdenum steels is not very strongly supported by the data, if the analyses of their few heats are carefully studied. Steel C1 has higher silicon and chromium than C5, which may easily account for the differences in oxidation resistance. These differences cannot, therefore, be ascribed entirely to the titanium content of C5, and anyway they are not much greater than the differences between the titanium and columbium steels which the authors say are negligible. The great difference in silicon content between steels C3 and C7 completely invalidates the comparison of the oxidation resistances of these steels on the basis of the titanium content, in view of the important effect that silicon is known to exert on this property. This again is an instance of the danger of drawing misleading conclusions from data on too few heats. Our own data on oxidation resistance of these 5 per cent chromium-molybdenum steels have indicated a beneficial effect of titanium, as did those of Norwood in METAL PROGRESS for March, 1934, p. 17. For instance, in the low silicon grade of this steel we found the following losses in weight by scaling for 1000 hours at 1500 degrees Fahr. (815 degrees Cent.): with columbium 2.2 grams per square inch, with titanium 0.41, and with neither 0.46. And in the high silicon grade the scale loss in 1000 hours at 1700 degrees Fahr. (925 degrees Cent.) was 10.15 grams per square inch with no titanium, 10.03 with 0.37 per cent titanium, 9.05 with 0.50 per cent columbium, 8.82 with 0.90 per cent titanium, and only 0.16 gram with 1.65 per cent titanium. This certainly does not support the authors' statement that titanium increases the amount of oxidation of this steel at 1700 degrees Fahr. (925 degrees Cent.), which I believe will be found incorrect by an impartial evaluation of all the available data.

### Oral Discussion

J. J. KANTER:[1] I would like to make a few remarks in reinforcement of Mr. Rohrig's discussion. Several years ago in the Crane Research Laboratories, Glen Guarnieri was engaged in studying the air oxidation rates of a series of alloy steels. It was soon apparent that consistent results could not be obtained by just putting specimens in the furnace and letting them scale at constant temperature. The conclusion was reached that variations in humidity in the air were responsible for erratic scaling rates. An apparatus was devised whereby various degrees of humidity could be constantly maintained, in which more concordant rates were measured. The normal variations of atmospheric humidity, it was demonstrated, can cause the air oxidation rate to vary several-fold. With this apparatus it was also possible to completely displace the air and run the humidity up to 100 per cent of water vapor. The results in 100 per cent of water vapor under practically no pressure were shown to check the oxidation rates obtained in high pressure steam. In view of our experience with the normal variations of air oxidation tests, we would not be inclined to ascribe much significance to some of the small orders of difference between the oxidation rates observed by the authors for various compositions of steel.

[1]Materials Research Engineer, Crane Co., Chicago.

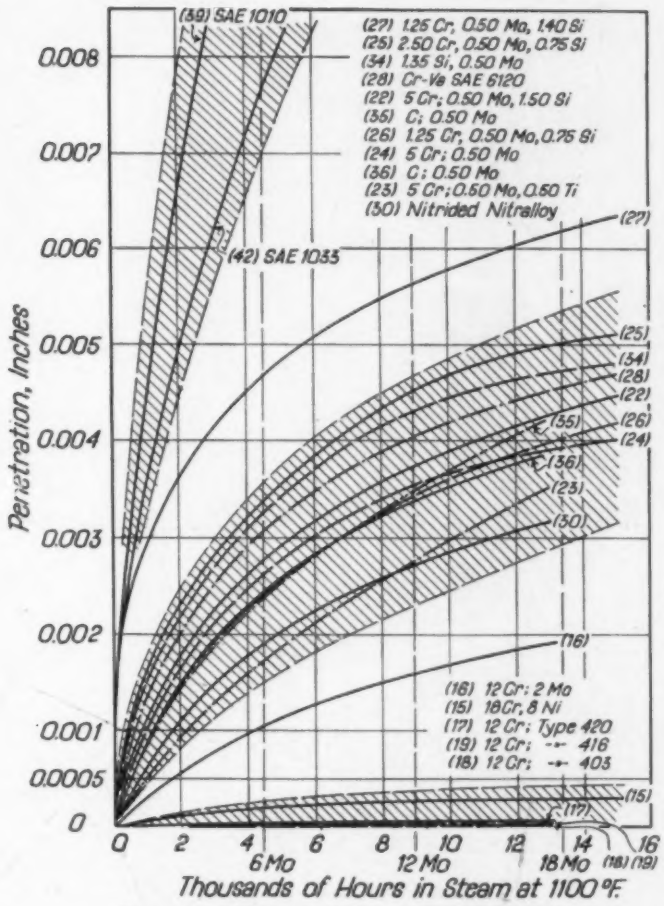


Fig. A—Effect of Long-Time Exposure to Steam at 1100 Degrees Fahr. Upon Carbon and Alloy Steel Bars.

I. A. ROHRIG:[2] The paper by Messrs. Miller, Benz, and Day is timely and presents much that is of great importance to those industries utilizing steels at high temperatures.

A review of the paper, however, prompts the observation that general conclusions respecting the scaling resistance of steels should not be drawn from studies in which the steels are subjected to only one reactive environment.

Experience gained in the operation of two experimental installations in the plants of The Detroit Edison Co., utilizing steam at high temperature, led to an investigation of the corrosive effects of flowing steam at both 925 and 1100 degrees Fahr. (495 and 595 degrees Cent.) on a group of materials that could be used for superheaters, piping and turbines. The results of that investigation, which was carried on for nearly 7 years, are the basis of a paper to be presented at the forthcoming annual meeting of the American Society of Mechanical Engineers. Certain of those results may be considered appropriately with those presented by Messrs. Miller, Benz, and Day.

Our studies have indicated, in the case of some alloys, the rate of corrosion in steam is definitely different from reported rates of oxidation in air.

[2]Research Department, The Detroit Edison Co., Detroit.

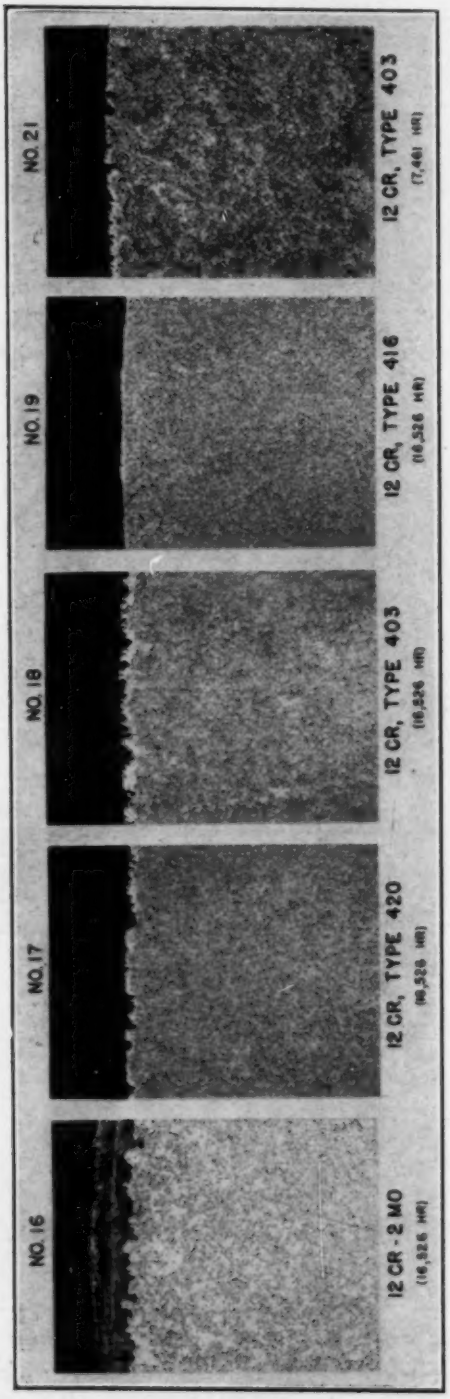


Fig. B—Photomicrographs of Surface Condition of 12 Per Cent Chromium Steels After Exposure to 1100 Degrees Fahr. Steam. × 35.

The authors conclude that at 1100 degrees Fahr. (595 degrees Cent.), the amount of oxidation for plain carbon, carbon-molybdenum, and 1 to 3 chro-

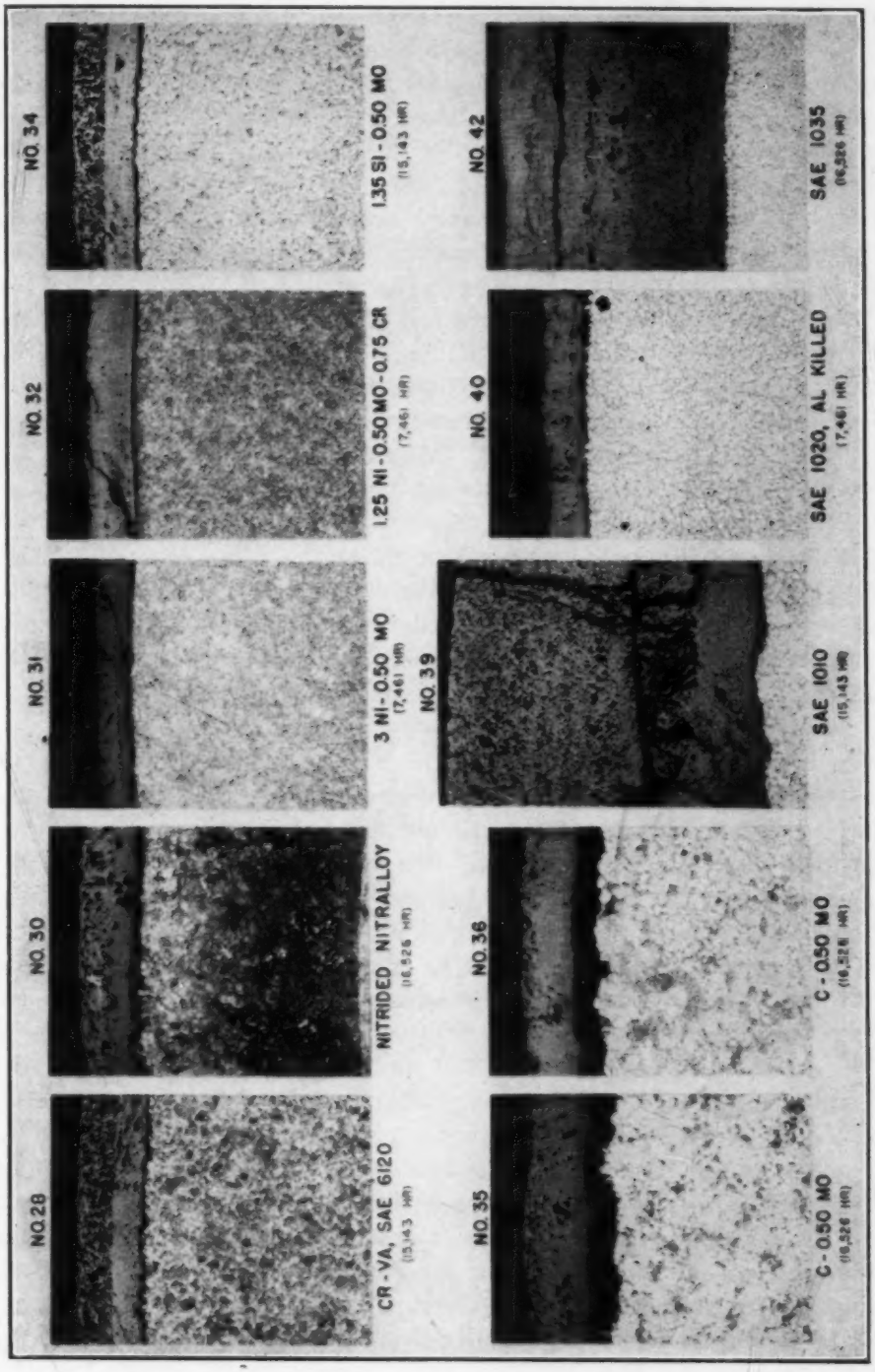


Fig. C—Photomicrographs of Surface Condition of Mild Alloy and Carbon Steels After Exposure to 1100 Degrees Fahr. Steam. × 35.

mium-molybdenum steels is about the same. This is in contrast to our observations in which it was found that for extended exposure (up to 16,000 hours in steam at 1100 degrees Fahr. (595 degrees Cent.), there is a definite retardation in the rate of metal loss in the case of the low-alloy steels. The

behavior of the plain carbon steels, however, was found to be about the same for steam corrosion as has been reported for air oxidation in that with prolonged exposure the loss due to scaling continues at a high rate as shown in Fig. A. The curves in this figure show that with the addition of as little as 0.50 per cent of molybdenum, the rate of corrosion of a steel in steam at 1100 degrees Fahr. (595 degrees Cent.) is lower than without that addition which is in contrast to what occurs in air oxidation at this temperature, as reported by the authors. Moreover, steels containing 0.50 per cent of molybdenum exhibit a corrosion rate approximately the same as that for steels containing up to 5.0 per cent of chromium with additions of molybdenum, silicon, or titanium.

Steels containing 12 per cent of chromium were among the best of the materials tested and indicate that chromium, without the addition of other alloying elements, is capable of imparting high corrosion resistance to steels exposed to high-temperature steam. The addition of 2 per cent of molybdenum to a 12 per cent chromium steel lowered the corrosion resistance of the alloy as shown in Fig. A.

The surface condition of 12 per cent chromium steels, after test, is shown by Fig. B. In most cases, the straight chromium stainless steels can be expected to pit when exposed to high temperature steam. The only one that had scaled was the sample that contained 2 per cent of molybdenum and the best of the group was a sample made of a high sulphur free-machining grade of 12 per cent chromium steel.

The beneficial effects of alloy additions in lessening the corrosive attack under the influence of steam at 1100 degrees Fahr. (595 degrees Cent.) is shown by the varying amount of scale on the steels shown in Fig. C.

In steam corrosion it was found that the formation and maintenance of an adherent scale materially increased the corrosion resistance of materials. Furthermore, it appears that the formation of a protective scale during high-temperature service can be controlled by using or limiting certain elements in an alloy; as for example, 0.50 per cent of molybdenum added to a plain carbon steel greatly improves the corrosion resistance in steam at 1100 degrees Fahr. (595 degrees Cent.), but 2.0 per cent of molybdenum added to a 12.0 per cent chromium steel appears to lower the scaling resistance in steam. Silicon can be considered in the same way in that a high silicon content appears not to improve the scaling resistance of steels in steam as it does in air.

The greatest rate of attack occurs during the early stages of the exposure whether the environment be high-temperature steam or air. Also, it is probable that the shape of the rate-loss curve for air oxidation may be approximately the same as for steam corrosion. The total amount of scale formed or the amount of metal lost in the two reactive mediums might be materially different.

### Authors' Closure

In replying to the discussion, the authors wish to express their appreciation of the comments received. Mr. Comstock has called attention to the difference in titanium-to-carbon and columbium-to-carbon ratio, and suggested that air hardening may have been responsible for the improved creep strength

of the hot-rolled and tempered 5 Cr-Mo-Cb steel. This seems reasonable, and we agree that it would be interesting to examine the creep behavior of a 5 Cr-Mo-Ti steel with a low titanium-to-carbon ratio. While there may be some doubt regarding the comparability of some of the 5 Cr-Mo steels, the tests indicate quite clearly that titanium or columbium does not produce any significant improvement in the scaling resistance of 5 Cr-Mo steel.

The authors are in accord with Mr. Rohrig's statement that "..... general conclusions respecting the scaling resistance of steels should not be drawn from studies in which the steels are subjected to only one reactive environment." It was for this reason that we emphasized that our tests had been made in air. No doubt results different from those obtained in air or steam would be encountered in the gaseous products of combustion of various types of fuels. The additional data presented by Mr. Rohrig are much appreciated and add greatly to the value of the paper.

In regard to the point raised by Mr. Kanter, we did not attempt to control the humidity beyond equipping the annular furnace with a muffle and sand seal. However, the furnace accommodated 40 specimens which were rotated at 1 rpm, and comparison of the behavior of the steels was limited to those which were tested together.

# AN EMERGENCY HEAT RESISTANT ALLOY

By Oscar E. Harder and James T. Gow

*Abstract*

*In an attempt to develop heat resistant alloys, low in scarce metals, for service up to 1400 degrees Fahr. (760 degrees Cent.), nearly 100 alloy compositions have been studied. The work included melting, casting, bend tests and tension tests at room temperature, tension and creep tests up to 1600 degrees Fahr. (870 degrees Cent.), and determination of the resistance of alloys to scaling in air and sulphur-bearing gases at temperatures of 1400 and 1600 degrees Fahr. (760 and 870 degrees Cent).*

*The most promising results have been found with an alloy containing about 0.30 to 0.35 per cent carbon, about 2 per cent silicon, with 10 to 12 per cent chromium, nickel in the range of 4 to 10 per cent, manganese in the range of 2 to 12 per cent, with the nickel and manganese supplementing each other and used in amounts to give a wholly austenitic alloy.*

*Data are given with reference to alloy composition, the relation of nickel and manganese contents at various chromium levels to ductility, and the amounts of manganese and nickel to produce a wholly austenitic alloy at different chromium levels. The most extensively studied alloy contained carbon 0.35 per cent, chromium 12.3 per cent, silicon 2.28 per cent, nickel 7.8 per cent, and manganese 7.8 per cent. This alloy was considered to have adequate strength, ductility, load-carrying capacity and resistance to oxidation at 1400 degrees Fahr. (760 degrees Cent.) and was wholly austenitic. Partially ferritic alloys, because of insufficient nickel and/or manganese, have lower strengths and lower L.C.S. values. Some comparisons were made between the properties of the emergency alloy and those of 18 per cent chromium - 8 per cent nickel and 25 per cent chromium - 12 per cent nickel.*

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A paper presented before the Twenty-fifth Annual Convention of the Society, held in Chicago, October 18 to 22, 1943. Of the authors, Oscar E. Harder is assistant director, and James T. Gow is assistant supervisor, Battelle Memorial Institute, Columbus, Ohio. Manuscript received July 9, 1943.

## Introduction

OVER a period of about two years, the Alloy Casting Institute has directed a considerable part of its research program at Battelle Memorial Institute to the development of what may be called an emergency heat resistant alloy. The authors are grateful to the Alloy Casting Institute and to Battelle Memorial Institute for permission to present a technical paper giving the results of this research.

Nickel became a scarce metal rather early in World War No. 2, and even before Pearl Harbor chromium was well up on the scarce metal list. This situation became more serious when the United States entered the war. Supplementary Order M-21-g, issued July 2, 1942, by the War Production Board, limited the chromium to 6 per cent, with no nickel, for temperatures between 900 and 1200 degrees Fahr. (480 and 650 degrees Cent.) and for some applications between 1200 and 1400 degrees Fahr. (650 and 760 degrees Cent.), and specified 18 per cent chromium-8 per cent nickel (18-8) for certain applications for temperatures between 1200 and 1400 degrees Fahr. (650 and 760 degrees Cent.). This order made alloys of only 6 per cent chromium and of the 18-8 type of special interest in the research program. Obviously it was desirable to develop an alloy or a group of alloys relatively low in nickel and chromium, and the Alloy Casting Institute chose to direct the research to finding an alloy which could be used over a limited temperature range, up to 1400 degrees Fahr. (760 degrees Cent.), with possibly limited use at slightly higher temperatures, such as 1500 and 1600 degrees Fahr. (815 and 870 degrees Cent.).

The general requirements for such an emergency alloy were listed under the following major headings:

1. Alloy Content. The alloy should be as low as possible in scarce metals, particularly nickel and chromium. Insofar as possible, the more scarce metals should be replaced by less scarce metals.

2. Ductility. The alloy should have sufficient ductility as-cast to provide safe handling in the foundry and to avoid the necessity of any heat treatment for handling and machining. Further, the alloy should not show excessive loss in ductility on heating at any temperature up to the maximum contemplated in service.

3. Strength and Load-Carrying Capacity. The strength of the alloy at 1400 degrees Fahr. (760 degrees Cent.) should, at least,

be equal to the strengths of established heat resistant alloys at their usual operating temperature, for example, the strength of the "HH" type alloys[1] at 1800 degrees Fahr. (980 degrees Cent.). This requirement applied both to short-time and long-time (creep) strength.

4. Structural Stability. In order for the alloy to meet the contemplated service requirements, it should be structurally stable at all operating temperatures, that is, it should not transform so as to become too hard and dangerously brittle, nor should it temper so as to lose its strength and load-carrying capacity. The coefficient of thermal expansion should be of the order of proven alloys, and there should be no significant change in dimensions in service.

5. Resistance to Oxidation. It was considered necessary for the alloy to have resistance to oxidation at the proposed operating temperatures equivalent to that of established heat resistant alloys at their usual operating temperatures. For example, the resistance to oxidation at 1400 and at 1600 degrees Fahr. (760 and 870 degrees Cent.) should be equivalent to the "HH" type alloy at 1800 and at 2000 degrees Fahr. (980 and 1095 degrees Cent.), respectively.

6. Melting and Casting. Finally, the alloy should not present special foundry problems in melting or in casting.

*Number of Alloys Studied*—About 90 different alloy compositions have been produced on a laboratory scale and studied. In addition, five alloys have been submitted by members of A.C.I. The amount of study given to a particular alloy composition has depended upon its promise in meeting the above-mentioned requirements. For example, some alloys could be discarded as of no further interest because they were so hard and brittle as-cast that they were nonmachinable and failed in the bend test. Others were so promising that they were carried through an extensive series of tests, including creep tests at 1400 and 1600 degrees Fahr. (760 and 870 degrees Cent.). Some of these more promising alloys were produced in duplicate heats and in larger heats.

The alloys were produced in four series, DA-DX, EA-EX, FA-FY, and GA-GT. Each group contained various compositions which were thought to have promise or which were of interest for comparison purposes, for example, alloys with 6 to 12 per cent chromium and 18 per cent chromium - 8 per cent nickel were of interest for comparison purposes. After a series had been tested, the compositions which definitely failed to meet the requirements

[1]Alloys of about 25 per cent chromium and 12 per cent nickel.

were dropped, the more promising compositions were modified, and a new series outlined, produced, and tested. The order of production and testing will not be used in the present paper, but rather the alloys will be grouped as to composition and their properties reported.

## Experimental Procedures

*Melting and Casting*—All alloys were melted in a high-frequency induction furnace with a magnesia crucible. Mild steel was used as the base, nickel was in the form of the metal, and chromium, manganese, and silicon were added as the ferro-alloys, except in the case of three alloys, FE-1, FH-1, and FX-1, in which silico-manganese was used.

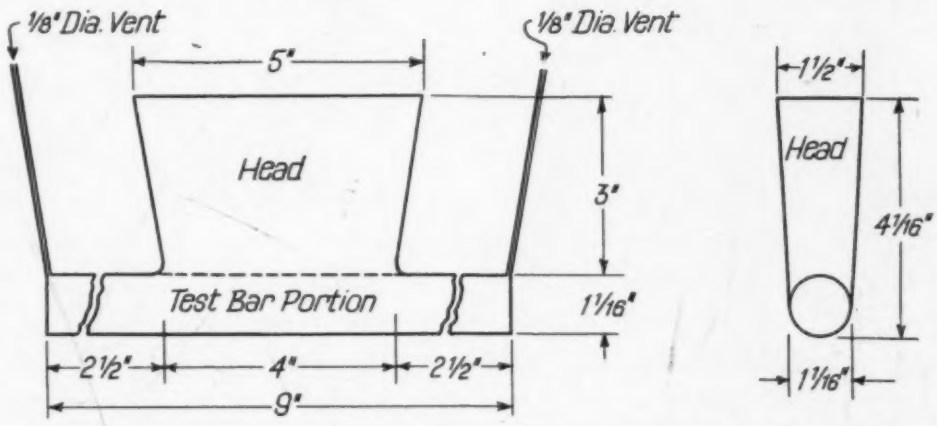


**Fig. 1—A.C.I. Tension Test Bar Casting.**

The castings were the A.C.I. tension test bar shown in Fig. 1 and a strip casting about 1 inch wide by 3/8 inch thick and about 10 inches in length for bend tests. All castings were poured in dry sand cores. No slag was used on the melts, and the only deoxidation was with silicon-calcium alloy equivalent to 0.05 per cent calcium.

*Bend Tests*—The bend tests were made on strip castings in the as-cast condition and after aging, which usually was 24 hours at 1400 degrees Fahr. (760 degrees Cent.), but longer aging times were also used. The specimens were machined on the tension side and bent in a jig around a mandrel of 2-inch diameter. Obviously, an alloy was to be rated as too brittle when it took little or no bend before fracturing. Those alloys which took a bend of 180 degrees were rated as satisfactory. For properties indicating promise, a

minimum angle of 30 degrees after aging 24 hours at 1400 degrees Fahr. (760 degrees Cent.) was selected.

*Short-Time Tension and Creep Tests*—Other testing procedures such as short-time tension tests at room and at elevated temperatures followed standard procedures and need not be described. The creep tests were in some cases made by the step-loading method, but when such a practice was used, it is shown by the curves and the tabulated data.

*Corrosion*—Oxidation tests were run by heating in air in an electric furnace, and at the end of the test the scale was removed by an electrolytic process in a fused salt bath. Scaling tests in sulphur-bearing gases will be described more in detail in the discussion of such tests later.

## Bend Tests

The compositions of the alloys and the results of bend tests are given in Tables I and II. When the compositions are given in round numbers, it generally means the intended composition for chromium, nickel, manganese, and silicon. The carbon contents were determined for most of the alloys, however. Because of the fact, as it will be brought out later, the most promising alloys were found to fall within certain narrow ranges in composition, alloys outside of this range in one or more elements are listed in Table I, while those within this range are listed in Table II. All of the alloys have been tested in the as-cast condition and after aging 24 hours at 1400 degrees Fahr. (760 degrees Cent.). In addition, some alloys have been tested after aging 500 hours at 1400 degrees Fahr. (760 degrees Cent.) and after aging 100 to 500 hours at 1200 degrees Fahr. (650 degrees Cent.).

The first two alloys in Table I, EA and EB, contain 6 per cent of chromium and no nickel. However, Alloy EA contained 0.5 per cent molybdenum, and Alloy EB contained 1.5 per cent copper. Alloy EA was extremely brittle as-cast and after aging 24 hours at 1400 degrees Fahr. (760 degrees Cent.), and EB took only a small bend as-cast and a still smaller bend after aging. Thus these two alloys which might be considered as representative of a composition covered by Supplementary Order M-21-g are indicated to be brittle. Tests to be reported later will show that these two alloys have relatively low resistance to oxidation at 1400 degrees Fahr. (760 degrees Cent.).

The microstructure of Alloy EA in the as-cast condition is shown in Fig. 2, and it will be noted that the structure is martensitic. The hardness was 514 Brinell. On aging 24 hours at 1400 degrees Fahr. (760 degrees Cent.) this alloy was annealed to such an extent that its hardness was only 255 Brinell.

Fig. 2—Photomicrograph of Alloy EA. As-Cast Condition. Carbon 0.30, Chromium 6.00, Manganese 1.00, Silicon 2.00, Molybdenum 0.5. A Fully Martensitic Structure. Brinell Hardness 514. × 500.

The next pair of alloys, EC and ED, were included because of interest in the properties of a 12 per cent chromium alloy with added molybdenum, and in addition, ED carried 1 per cent columbium. These alloys, at this carbon content, were brittle under all the testing conditions. Alloy EF contained 10 per cent chromium but in addition had 2 per cent of aluminum added. It was brittle. The next four alloys, DQ, DR, DS, and DT, are obviously eliminated from further consideration because of brittleness. The next eight alloys are modifications of the 6 per cent chromium alloy by the addition of nickel and manganese. When the nickel was 4 per cent and the manganese was increased to 15 per cent, the specimen even after aging took a full bend. When the nickel was 8 per cent with manganese in the range of 5 to 15 per cent, the specimens took a full bend

**Table I**

**Summary of Bend Test Results**

(Alloys Varying in One or More Elements from the Range of 0.33% C, 2% Si, 10-13% Cr, 4-10% Ni, 1-10% Mn)

| Alloy No. | Composition, Per Cent | | | | | As Cast | Aged 24 Hours at 1400 Degrees Fahr. | Aged 100 Hours at 1200 Degrees Fahr. |
|---|---|---|---|---|---|---|---|---|
| | Cr | Ni | Mn | Si | C | | | |
| EA (1) | 6 | .. | 1 | 2 | 0.30 | Broke 0 Degree Bend | Broke 0 Degree Bend | |
| EB (5) | 6 | .. | 1 | 1.5 | 0.20 | Broke 30 Degree Bend | Broke 15 Degree Bend | |
| EC (1) | 12 | .. | 0.5 | 2 | 0.30 | Broke 0 Degree Bend | Broke 0 Degree Bend | |
| ED (2) | 12 | .. | 0.5 | 2 | 0.30 | Broke 0 Degree Bend | Broke 5 Degree Bend | Broke 20 Degree Bend |
| EF (3) | 10 | .. | 1 | 1 | 0.30 | Broke 0 Degree Bend | Broke 10 Degree Bend | |
| DQ (4) | 10 | 2 | 2 | 1 | 0.30 | Broke 5 Degree Bend | Broke 0 Degree Bend | Broke 5 Degree Bend |
| DR (4) | 10 | 2 | 2 | 2 | 0.49 | Broke 30 Degree Bend | Broke 0 Degree Bend | Broke 0 Degree Bend |
| DS | .. | .. | 10 | 2 | 0.30 | Broke 5 Degree Bend | Broke 5 Degree Bend | |
| DT | .. | .. | 10 | 4 | 0.30 | Broke 0 Degree Bend | Broke 0 Degree Bend | Broke 0 Degree Bend |
| DA | 6 | 4 | 5 | 1 | 0.31 | Broke 45 Degree Bend | Broke 0 Degree Bend | |
| DB | 6 | 4 | 10 | 2 | 0.47 | Full Bend | Broke 5 Degree Bend | |
| DC | 6 | 4 | 15 | 1 | 0.29 | Full Bend | Full Bend | |
| DD | 6 | 8 | 5 | 1 | 0.30 | Full Bend | Full Bend | |
| EG | 6 | 8 | 5 | 2 | 0.30 | Full Bend | Broke 20 Degree Bend | |
| EH | 6 | 8 | 10 | 2 | 0.30 | Full Bend | Broke 90 Degree Bend | |
| DE | 6 | 8 | 10 | 2 | 0.51 | Full Bend | Broke 60 Degree Bend | |
| DF | 6 | 8 | 15 | 1 | 0.31 | Full Bend | Full Bend | |
| DG | 10 | 4 | 5 | 1 | 0.30 | Broke 60 Degree Bend | Broke 0 Degree Bend | |
| DH | 10 | 4 | 10 | 2 | 0.50 | Full Bend | Broke 0 Degree Bend | Broke 10 Degree Bend |
| DI | 10 | 4 | 15 | 1 | 0.31 | Full Bend | Full Bend | |
| EI | 10 | 6 | 10 | 2 | 0.50 | Full Bend | Broke 10 Degree Bend | Broke 20 Degree Bend |
| DJ | 10 | 8 | 5 | 1 | 0.31 | Full Bend | Full Bend | |

**Table I — (Continued)**

| Alloy No. | Composition, Per Cent | | | | | As Cast | Aged 24 Hours at 1400 Degrees Fahr. | Aged 100 Hours at 1200 Degrees Fahr. |
|---|---|---|---|---|---|---|---|---|
| | Cr | Ni | Mn | Si | C | | | |
| EK | 10 | 8 | 5 | 2 | 0.50 | Full Bend | Broke 30 Degree Bend | |
| EM (4) | 10 | 8 | 5 | 1 | 0.30 | Full Bend | Full Bend | |
| EN (4) | 10 | 8 | 5 | 2 | 0.30 | Full Bend | Full Bend | |
| DK | 10 | 8 | 10 | 2 | 0.59 | Full Bend | Broke 75 Degree Bend | Broke 30 Degree Bend |
| EL | 10 | 8 | 10 | 3 | 0.50 | Full Bend | Broke 15 Degree Bend | |
| DL | 10 | 8 | 15 | 1 | 0.32 | Full Bend | Full Bend | |
| DM | 12 | 6 | 1 | 1 | 0.53 | Full Bend | Broke 5 Degree Bend | |
| DN | 12 | 6 | 4 | 1 | 0.50 | Full Bend | Broke 5 Degree Bend | |
| EP | 12 | 6 | 4 | 2 | 0.50 | Full Bend | Broke 5 Degree Bend | |
| DO | 12 | 6 | 8 | 1 | 0.49 | Full Bend | Broke 30 Degree Bend | Broke 30 Degree Bend |
| DP | 12 | 6 | 8 | 2 | 0.49 | Full Bend | Broke 30 Degree Bend | Broke 15 Degree Bend |
| EQ | 12 | 6 | 8 | 3 | 0.50 | Broke 60 Degree Bend | Broke 5 Degree Bend | Broke 15 Degree Bend |
| ER | 12 | 6 | 10 | 2 | 0.50 | Full Bend | Broke 20 Degree Bend | Broke 10 Degree Bend |
| ES | 12 | 6 | 10 | 3 | 0.50 | Full Bend | Broke 0 Degree Bend | Broke 30 Degree Bend |
| ET | 12 | 6 | 10 | 4 | 0.50 | Broke 20 Degree Bend | Broke 0 Degree Bend | Broke 6 Degree Bend |
| DU (6) | 18 | 8 | 1 | 1 | 0.30 | Full Bend | Full Bend | Full Bend |
| DV (6) | 18 | 4 | 6 | 1 | 0.32 | Full Bend | Broke 30 Degree Bend | Broke 50 Degree Bend |
| EW | 18 | 6 | 6 | 2 | 0.30 | Full Bend | Broke 30 Degree Bend | |
| EV | 18 | 6 | 4 | 2 | 0.40 | Full Bend | Broke 15 Degree Bend | Broke 25 Degree Bend |
| EU | 18 | 4 | 6 | 2 | 0.40 | Broke 10 Degree Bend | Broke 12 Degree Bend | Broke 6 Degree Bend |
| EX | 18 | .. | 1 | 2 | 0.30 | Broke 0 Degree Bend | Broke 0 Degree Bend | Broke 10 Degree Bend |
| DW (6) | 18 | .. | 10 | 1 | 0.35 | Broke 20 Degree Bend | Broke 2 Degree Bend | Broke 20 Degree Bend |
| DX (6) | 24 | 12 | 1 | 1 | 0.38 | Full Bend | Full Bend | Full Bend |

(1) Also 0.5% Mo
(2) Also 0.5% Mo and 1% Cb
(3) Also 2% Al
(4) Also 2% Cu
(5) Also 1.5% Cu
(6) Intended N—0.07%

as-cast, but when the silicon was increased from 1 to 2 per cent, the ductility in the aged condition was decreased. While some of these alloys had adequate ductility with only 6 per cent chromium, they did not have the desired resistance to oxidation at 1400 degrees Fahr. (760 degrees Cent.). Alloys DG, DH, and DI are representative of those containing 10 per cent chromium and 4 per cent nickel with varying manganese. Again it is indicated that when there is sufficient manganese present, the alloys take a full bend. However, increasing the silicon from 1 to 2 per cent or the carbon from around 0.30 to 0.50 per cent decreases ductility. Alloy EI is considered to have low ductility because of the combination of high silicon and high carbon. The next group of seven alloys, DJ to DL, have 10 per cent chromium and 8 per cent nickel with variations in manganese, silicon, and carbon. In addition, EM and EN contained 2 per cent of copper. Alloy EL was relatively brittle on aging and that was attributed to its silicon content of 3 per cent. The next group of alloys contained 12 per cent chromium and 6 per cent nickel with variations in manganese and silicon but with the carbon on the high side at about 0.50 per cent. It is indicated that for this chromium and nickel content, the manganese needs to be about 8 per cent when the silicon is 1 per cent. Increasing the silicon from 1 to 2 per cent reduces the ductility somewhat for Alloy DP. The effect of silicon content is shown in a more pronounced way for Alloys ER, ES, and ET where the silicon varied from 2 to 4 per cent. With 4 per cent silicon, the alloy was relatively brittle as-cast.

The bend test specimens of the D series are shown in Fig. 3. Reference should be made to Table I for composition.

Alloy DU is representative of the 18-8 type, only that the carbon content of 0.30 per cent may be somewhat higher than would generally be used in castings for heat resistant purposes. However, this alloy took a full bend under all conditions of test. DV is a modification of this alloy with decreased nickel and increased manganese and with lower ductility on aging. Other modifications of 18-8 are shown in Alloys EW, EV, and EU, and in all cases they are less ductile than the regular alloy. EX is an 18 per cent chromium alloy, while DW is an 18 per cent chromium - 10 per cent manganese alloy. Both of these alloys were low in ductility. DX is representative of the "HH" type alloy with the chromium, nickel, and carbon of such proportion as to give a wholly austenitic alloy. The specimens took a full bend under all conditions of heat treatment.

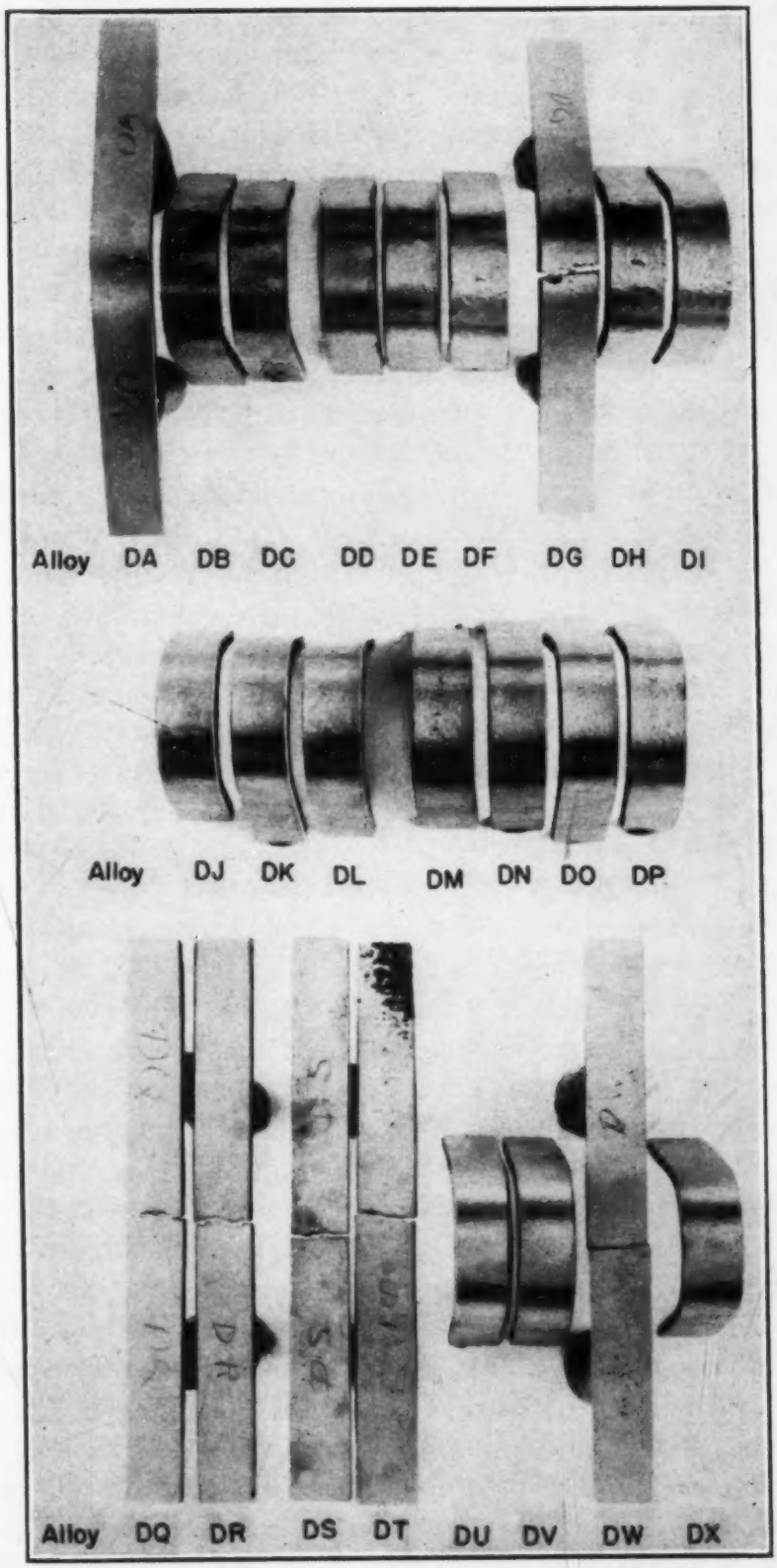


Fig. 3—Bend-Tested Specimen of D-Series Alloys.

In addition to being brittle in the bend test, some of the alloys listed in Table I failed to meet requirements because of high hardness in the as-cast condition. Alloys EA, EB, EC, and ED fall in this class. They are martensitic as cast with hardnesses of 514, 429, 578, and 495, respectively. Other alloys which had somewhat lower hardness as cast but yet were sufficiently hard to be difficult to machine are Alloys EX, with hardness of 305; DQ, 326; DS, 400; and DT, 371. The high hardness in the cast condition in addition to low ductility in the bend test tended to disqualify these alloys for the intended application. To be sure, some of these alloys could be heat treated to make them machinable, but because of their tendency to form martensite, they would be likely to be embrittled in service, especially if cooled relatively rapidly. In addition to the alloys which are brittle and of high hardness as-cast, certain alloys were austenitic as-cast but transformed on aging to the martensitic structure of high hardness, and the alloys became brittle. Representative of this are Alloys DA, which developed a hardness of 361 Brinell; DM, 437; DG, 302; and DR, 377. Evidently these alloys would not meet the proposed requirements because of becoming hard and embrittled in service. Alloy DM had a hardness of only 163 as cast but on aging 24 hours at 1400 degrees Fahr. (760 degrees Cent.), its hardness increased to 437 and changed from a full bend as-cast to only a 5-degree bend after aging.

The alloys listed in Table II fall within a comparatively narrow range of composition with the carbon about 0.30 to 0.35, chromium 10 to 13, nickel 4 to 10, and manganese 1 to 10. The intended silicon content was about 2 per cent because the early work indicated that increasing the silicon from 1 per cent or under to about 2 per cent improved corrosion resistance, but when the silicon was further increased to 3 to 4 per cent, there was significant loss in ductility. Alloy GB is below the carbon range with only 0.24 per cent.

As will be evident from this table, chromium has been studied at levels of 10, 11, 12, and 13 per cent with nickel and manganese as variables. As will be brought out later, it is necessary to adjust the nickel and manganese contents for each chromium level to produce a wholly austenitic alloy, that the nickel and manganese are supplementary but not equivalent in producing austenitic structures, and that more nickel and manganese are required at the 10 per cent chromium level than at the 12 per cent chromium level. The alloys presented in Table I and in Table II served as the experimental

alloys to help establish these relations which are mentioned at this time because they are necessary in discussing the results of the bend test.

In the series of alloys of 10 per cent chromium and 6 per cent nickel the ductility of the alloys, as determined by the bend test, increases with increase in manganese content. The same relation is found in the series containing 7, 8, and 9 per cent nickel. In the series containing 11 per cent chromium, it is again shown that the trend is for the ductility in the bend test at any nickel level to increase with the manganese content. In these alloys there is a trend, for those which are not stable austenite, for the ductility to fall off on aging 24 hours at 1400 degrees Fahr. (760 degrees Cent.) and especially if the aging time is extended from 300 to 500 hours. On the other hand, such alloys as GB and GBA took a full bend after aging 500 hours at 1200 degrees Fahr. (650 degrees Cent.), which temperature has been established as more damaging to ductility than 1400 degrees Fahr. (760 degrees Cent.). At the 12 per cent chromium level, alloys are shown for nickel levels of 6, 7, 8, 9, and 10 with variable manganese contents. At any nickel level, the ductility showed a trend to increase as the manganese content increased. For a given manganese content, the higher the nickel content the more likely the specimen was to take a full bend. For 12 per cent chromium at the 6 per cent nickel level, more than 9 per cent manganese was required to make the specimen take a full bend after aging 24 hours at 1400 degrees Fahr. (760 degrees Cent.). However, at the 7 per cent nickel level only 8 per cent of manganese is sufficient for this purpose. With 8 per cent nickel only 3 per cent manganese was required to make the specimen take a full bend after the aging test, but there was loss of ductility when the aging time was extended to 500 hours. However, the specimens containing 4 or more per cent of manganese at this chromium-nickel level took a bend of 50 degrees or more even after aging 500 hours at 1400 degrees Fahr. (760 degrees Cent.). The data in Table II serve to indicate the relation of the required amounts of nickel and manganese for alloys of this chromium content to the ductility of as-cast and aged specimens. Further differentiation among these alloys was obtained by tension tests at room temperature on specimens which had been aged 24 hours at 1400 degrees Fahr. (760 degrees Cent.) and, in some cases, specimens which had been aged at intermediate temperatures, more particularly at 1200 degrees Fahr. (650 degrees Cent.), for

**Table II**
**Summary of Bend Test Results**

(Alloys of .30-.35% C, 10-13% Cr, 4-10% Ni, 1-10% Mn, 2% Si)

| Alloy No. | Composition, Per Cent | | | | | As Cast | Aged 24 Hours at 1400 Degrees Fahr. | Aged 500 Hours at 1400 Degrees Fahr. (1) | Aged 500 Hours at 1200 Degrees Fahr. |
|---|---|---|---|---|---|---|---|---|---|
| | Cr | Ni | Mn | Si | C | | | | |
| FY | 10 | 6 | 3 | 2 | 0.33 | Broke 55 Degree Bend | Broke 25 Degree Bend | Broke 2 Degree Bend | |
| FA | 10 | 6 | 6 | 2 | 0.32 | Full Bend | Broke 25 Degree Bend | Broke 25 Degree Bend | |
| FB | 10 | 6 | 7 | 2 | 0.33 | Broke 40 Degree Bend | Broke 40 Degree Bend | Broke 20 Degree Bend | |
| FC | 10 | 6 | 8 | 2 | 0.33 | Full Bend | Broke 15 Degree Bend | Broke 35 Degree Bend | |
| FD | 10 | 6 | 9 | 2 | 0.33 | Full Bend | Full Bend | Broke 50 Degree Bend | |
| FE-1 | 10 | 7.0 | 6.1 | 1.92 | 0.32 | Full Bend | Full Bend | | Broke 20 Degree Bend |
| FE | 10.2 | 6.9 | 5.6 | 2.07 | 0.32 | Full Bend | Broke 60 Degree Bend | Broke 30 Degree Bend | |
| GA | 9.9 | 7.1 | 6.0 | 2.6 | 0.36 | Full Bend | Broke 50 Degree Bend | Broke 30 Degree Bend | Broke 10 Degree Bend |
| FF | 10 | 7 | 7 | 2 | 0.32 | Full Bend | Full Bend | Broke 50 Degree Bend | |
| FG | 10 | 7 | 8 | 2 | 0.33 | Full Bend | Full Bend | Broke 85 Degree Bend | |
| GC | 10 | 8 | 3.0 | 2.16 | 0.33 | Full Bend | Full Bend | | Broke 30 Degree Bend |
| FH | 9.5 | 7.6 | 4.6 | 1.92 | 0.32 | Broke 120 Degree Bend | Broke 20 Degree Bend | Broke 15 Degree Bend | |
| FH-1 | 9.8 | 8.1 | 5.3 | 2.04 | 0.32 | Full Bend | Full Bend | | Broke 50 Degree Bend |
| EJ | 10 | 8 | 5 | 2 | 0.32 | Full Bend | Broke 45 Degree Bend | | |
| FI | 10.3 | 7.8 | 5.7 | 2.16 | 0.33 | Full Bend | Broke 45 Degree Bend | Broke 50 Degree Bend | |
| FJ | 10 | 8 | 7 | 2 | 0.31 | Full Bend | Full Bend | Broke 40 Degree Bend | |
| FK | 10 | 8 | 8 | 2 | 0.33 | Full Bend | Full Bend | Broke 40 Degree Bend | |
| GD | 10 | 9 | 3 | 2 | 0.33 | Full Bend | Full Bend | | Broke 50 Degree Bend |
| GE | 10 | 9 | 5 | 2 | 0.33 | Full Bend | Full Bend | | Broke 50 Degree Bend |
| GL | 11 | 7 | 2 | 2 | 0.33 | Full Bend | Broke 30 Degree Bend | Broke 8 Degree Bend* | |
| GM | 11 | 7 | 4 | 2 | 0.33 | Full Bend | Broke 20 Degree Bend | Broke 28 Degree Bend* | |
| FL | 11 | 7 | 6 | 2 | 0.33 | Full Bend | Broke 95 Degree Bend | Broke 30 Degree Bend | |
| FM | 11 | 7 | 7 | 2 | 0.33 | Full Bend | Full Bend | Broke 45 Degree Bend | |
| GN | 11 | 8 | 1 | 2 | 0.33 | Full Bend | Broke 38 Degree Bend | Broke 13 Degree Bend* | |
| GO | 11 | 8 | 3 | 2 | 0.33 | Full Bend | Broke 44 Degree Bend | Broke 27 Degree Bend* | |
| GP | 11 | 9 | 1 | 2 | 0.33 | Full Bend | Broke 40 Degree Bend | Broke 22 Degree Bend* | |
| GQ | 11 | 9 | 2 | 2 | 0.33 | Full Bend | Full Bend | Broke 40 Degree Bend | |

**Table II—(Continued)**

| Alloy No. | Composition, Per Cent Cr | Ni | Mn | Si | C | As Cast | Aged 24 Hours at 1400 Degrees Fahr. | Aged 500 Hours at 1400 Degrees Fahr. (1) | Aged 500 Hours at 1200 Degrees Fahr. |
|---|---|---|---|---|---|---|---|---|---|
| GR | 11 | 10 | 1 | 2 | 0.33 | Full Bend | Full Bend | Broke 48 Degree Bend* | |
| EO | 12 | 4 | 10 | 2 | 0.30 | Full Bend | Broke 5 Degree Bend | | |
| FN | 12 | 6 | 6 | 2 | 0.33 | Full Bend | Broke 50 Degree Bend | Broke 20 Degree Bend | |
| FO | 12 | 6 | 7 | 2 | 0.33 | Full Bend | Broke 35 Degree Bend | Broke 25 Degree Bend | |
| FP | 12 | 6 | 8 | 2 | 0.32 | Full Bend | Broke 60 Degree Bend | Broke 40 Degree Bend | |
| FQ | 12 | 6 | 9 | 2 | 0.33 | Full Bend | Broke 105 Degree Bend | Broke 20 Degree Bend | |
| FR | 12 | 7 | 5 | 2 | 0.33 | Full Bend | Broke 60 Degree Bend | Broke 45 Degree Bend | |
| FS | 12 | 7 | 6 | 2 | 0.33 | Full Bend | Broke 90 Degree Bend | Broke 30 Degree Bend | |
| FT | 12 | 7 | 8 | 2 | 0.33 | Full Bend | Full Bend | Broke 50 Degree Bend | |
| GF | 12 | 8 | 3 | 2 | 0.33 | Full Bend | Full Bend | Broke 15 Degree Bend | |
| FU | 12 | 8 | 4 | 2 | 0.33 | Full Bend | Full Bend | Broke 50 Degree Bend | |
| FV | 12 | 8 | 5 | 2 | 0.33 | Full Bend | Full Bend | Broke 50 Degree Bend | |
| FW | 12 | 8 | 6 | 2 | 0.33 | Full Bend | Full Bend | Broke 70 Degree Bend | |
| FX | 11.4 | 7.9 | 6.7 | 1.77 | 0.32 | Full Bend | Full Bend | Broke 50 Degree Bend | |
| GK | 12.3 | 7.8 | 7.8 | 2.28 | 0.35 | Full Bend | Full Bend | | Broke 25 Degree Bend |
| FX-1 | 11.9 | 8.1 | 8.0 | 2.02 | 0.32 | Full Bend | Full Bend | | Broke 40 Degree Bend |
| GH | 12 | 9 | 3 | 2 | 0.33 | Full Bend | Full Bend | | Broke 60 Degree Bend |
| GG | 12 | 9 | 4 | 2 | 0.33 | Full Bend | Full Bend | | Full Bend |
| GI | 12 | 10 | 3 | 2 | 0.33 | Full Bend | Full Bend | | Broke 30 Degree Bend |
| GJ | 12 | 10 | 5 | 2 | 0.33 | Full Bend | Full Bend | | Broke 40 Degree Bend |
| GB | 13.1 | 9 | 9.2 | 1.59 | 0.24 | Full Bend | Full Bend | | Full Bend |
| GB-A | 13 | 9 | 9 | 1.5 | 0.30 | Full Bend | Full Bend | | Full Bend |

NOTE: (1) The starred (*) alloys listed under the column headed Aged 500 Hours at 1400 degrees Fahr. were aged only 300 hours at 1400 degrees Fahr.

periods of time up to 500 hours. These tests were necessary to classify the alloys as to structural stability and their tendency to transform. In this paper, an alloy will be classed as wholly austenitic when it is nonmagnetic as-cast and nonmagnetic after aging 24 hours at 1400 degrees Fahr. (760 degrees Cent.). The term stably austenitic will generally be used to indicate alloys which remain nonmagnetic even in the deformed sections, as in the tension test, after being aged for long periods of time at temperatures up to and including 1400 degrees Fahr. (760 degrees Cent.). Thus alloys which are classed as wholly austenitic may not be entirely stably austenitic under all possible conditions of testing or of service. These relations will be brought out more in detail in the discussion of tension tests and the accompanying magnetic properties.

## Tensile Properties of the Alloys

Tension tests have been used as a means of determining the suitability of the various alloys for the intended application. Because of the extensive use of tension tests at room temperature using alloys which had been aged 24 hours at 1400 degrees Fahr. (760 degrees Cent.) and the fact that these alloys were intended for service at that temperature, all of the tension tests at room temperature were made on aged specimens. Extensive use has been made of tension tests at 1400 degrees Fahr. (760 degrees Cent.), again using specimens which had been aged 24 hours at 1400 degrees Fahr. (760 degrees Cent.). The results of these tests are given in Tables III and IV.

Table III gives the same group of alloys as reported in Table I for the bend tests. They are alloys which depart from the limited range in composition of the alloys included in Tables II and IV. Again Table III includes the 6 per cent chromium alloy, EA, and an 18-8 alloy, DU. It also includes an alloy of the "HH" type (DX) for comparison purposes. In a number of cases, tension tests were not made at room temperature because the alloy had been eliminated from the group of promising alloys for failure in the bend test or for lack of resistance to oxidation. In some cases, however, tests were made at 1400 degrees Fahr. (760 degrees Cent.) in order to determine the high temperature strength of the alloy. Table III also gives the magnetic characteristics of the alloys. The first five alloys in this table are ferritic, at least under some conditions, and are strongly magnetic. They could not be tested with the equip-

**Table III**

**Summary of Tension Test Data and the Ferro-Magnetic Character for Alloys Varying in One or More Elements from the Range of 0.33% C, 2% Si, 10-13% Cr, 4-10% Ni, 1-10% Mn**

| Alloy No. | Composition Per Cent Cr | Ni | Mn | Si | C | Tests at Room Temperature: Tensile Strength Psi. | Yield Strength Psi. | Elong. in 2" Per Cent | Red. of Area Per Cent | Tests at 1400° F.: Tensile Strength Psi. | Yield St'gth 0.2% Def. Psi. | Elong. in 2" Per Cent | Red. of Area Per Cent | Ferro-Magnetic Character of Alloys: Broken in Tension at Room Temp. Threaded Section | Reduced Section | Broken in Tension at 1400° F. Threaded Section | Reduced Section |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| EA (1) | 6 | . | 1 | 2 | 0.30 | ..... | ..... | .... | .... | 9,400 | ..... | 44 | 76 | .. | .. | .. | .. |
| EB (5) | 6 | . | 1 | 1.5 | 0.20 | ..... | ..... | .... | .... | 14,000 | ..... | 32 | 57 | .. | .. | .. | .. |
| EC (1) | 12 | . | 0.5 | 2 | 0.30 | ..... | ..... | .... | .... | 17,600 | ..... | 46 | 91 | .. | .. | .. | .. |
| ED (2) | 12 | . | 0.5 | 2 | 0.30 | ..... | ..... | .... | .... | 18,600 | ..... | 40 | 82 | .. | .. | .. | .. |
| EF (3) | 10 | . | 1 | 1 | 0.30 | ..... | ..... | .... | .... | 10,400 | ..... | 85 | 94 | .. | .. | .. | .. |
| EG | 6 | 8 | 5 | 2 | 0.30 | ..... | ..... | .... | .... | 20,900 | 16,200 | 16.5 | 10.7 | .. | .. | N | W |
| EH | 6 | 8 | 10 | 2 | 0.30 | ..... | ..... | .... | .... | 23,400 | 18,700 | 26.0 | 24.4 | .. | .. | N | N |
| DH | 10 | 4 | 10 | 2 | *0.50* | 74,800 | 52,500 | 3.5 | 3.9 | 33,400 | 23,400 | 13.5 | 17.0 | N (1.01) | N | N | N |
| EI | 10 | 6 | 10 | 2 | 0.50 | ..... | ..... | .... | .... | 32,400 | 23,000 | 15.0 | 15.6 | .. | .. | W ? | W ? |
| DJ | 10 | 8 | 5 | 1 | *0.31* | 74,700 | 38,000 | 25.0 | 25.8 | 21,000 | 15,300 | 28.5 | 32.8 | N | VW | N | N |
| EK | 10 | 8 | 5 | 2 | 0.50 | ..... | ..... | .... | .... | 33,600 | 23,200 | 12.0 | 15.9 | .. | .. | N (1.03) | N |
| EM (4) | 10 | 8 | 5 | 1 | 0.30 | ..... | ..... | .... | .... | 25,500 | 17,800 | 7.0 | 8.1 | .. | .. | N | N |
| EN (4) | 10 | 8 | 5 | 2 | 0.30 | ..... | ..... | .... | .... | 26,200 | 21,700 | 7.5 | 8.1 | .. | .. | N | N |
| DK | 10 | 8 | 10 | 2 | 0.50 | 103,200 | 48,000 | 14.0 | 14.5 | 31,900 | 23,600 | 7.0 | 24.8 | N | N | .. | .. |
| EL | 10 | 8 | 10 | 3 | 0.50 | ..... | ..... | .... | .... | 29,700 | 23,800 | 24.0 | 43.7 | .. | .. | N (1.00) | N |
| DN | 12 | 6 | 4 | 1 | *0.50* | 89,100 | 50,500 | 9.0 | 7.7 | 36,400 | 21,000 | 14.0 | 13.7 | VW | M | VW | VW |
| EP | 12 | 6 | 4 | 2 | 0.50 | ..... | ..... | .... | .... | 33,500 | 22,800 | 14.0 | 18.4 | .. | .. | W | W |
| DO | 12 | 6 | 8 | 1 | 0.49 | 95,200 | 51,500 | 10.0 | 11.5 | 35,300 | 21,200 | 14.0 | 26.8 | N | N | N | N |
| DP | 12 | 6 | 8 | 2 | *0.49* | 82,700 | 52,500 | 5.0 | 5.4 | 50,200 | 23,500 | 12.5 | 22.7 | N | N | VW | VW |
| EQ | 12 | 6 | 8 | 3 | 0.50 | ..... | ..... | .... | .... | 30,000 | 23,700 | 26.0 | 44.0 | .. | .. | N | N |
| ER | 12 | 6 | 10 | 2 | 0.50 | ..... | ..... | .... | .... | 32,200 | 22,400 | 12.5 | 13.7 | .. | .. | N | VW |
| ES | 12 | 6 | 10 | 3 | 0.50 | ..... | ..... | .... | .... | 29,400 | 23,400 | 21.0 | 24.8 | .. | .. | N (1.00) | N |
| ET | 12 | 6 | 10 | 4 | 0.50 | ..... | ..... | .... | .... | 28,500 | 21,200 | 40.5 | 51.7 | .. | .. | N | VW |
| DU | 18 | 8 | 1 | 1 | *0.30* | 97,100 | 45,000 | 25.5 | 20.6 | 30,500 | 19,500 | 13.5 | 19.5 | N (1.00) | M (1.22) | VW | VW |
| DV | 18 | 4 | 6 | 1 | *0.32* | 93,400 | 44,000 | 16.5 | 16.3 | 32,200 | 22,600 | 26.0 | 29.5 | N (1.03) | W (1.06) | N | .. |
| EW | 18 | 6 | 6 | 2 | 0.30 | ..... | ..... | .... | .... | 25,600 | 20,800 | 28.0 | 31.8 | .. | .. | N | N |
| EV | 18 | 6 | 4 | 2 | 0.40 | ..... | ..... | .... | .... | 43,500 | ..... | 15.0 | 17.7 | .. | .. | VW | W |
| EU | 18 | 4 | 6 | 2 | 0.40 | ..... | ..... | .... | .... | 35,900 | 24,500 | 10.0 | 24.1 | .. | .. | W | W |
| EX | 18 | . | 1 | 2 | 0.30 | ..... | ..... | .... | .... | 10,700 | 8,500 | 56.0 | 91.8 | .. | .. | SM | SM |
| DX | 24 | 12 | 1 | 1 | *0.36* | 97,600 | 49,000 | 18.5 | 16.3 | 32,700 | ..... | 18.0 | 21.6 | N | N | N | N |

(1) Also 0.5% Mo. (2) Also 0.5% Mo, 1% Cb. (3) Also 2% Al. (4) Also 2% Cu. (5) Also 1.5% Cu.

ment which was used because it is limited to a magnetic permeability of 4.5.

The 6 per cent chromium alloy, EA, has low strength at 1400 degrees Fahr. (760 degrees Cent.). As a rough approximation, it has only about one-third the strength for the average of the other alloys. Adding copper to this alloy, as in the case of EB, increased the strength substantially but only to about one-half that of the average of the other alloys. Twelve per cent chromium alloys with the addition of molybdenum, and molybdenum and columbium are substantially higher in strength but yet much below the other alloys listed in this table or those shown in Table IV. The 10 per cent chromium alloy, EF, with 2 per cent aluminum also was low in strength. Tests on Alloy EA indicate such low strength as to be a serious limitation on its use at a temperature of 1400 degrees Fahr. (760 degrees Cent.). Another alloy low in strength is EX which is a ferritic 18 per cent chromium alloy. For the remainder of the alloys the strength seems to be adequate both at room temperature and at 1400 degrees Fahr. (760 degrees Cent.). A relatively small number of the alloys tested are low in ductility at room temperature. However, many of these alloys were not tested in tension at room temperature because they were too hard to machine or they had been shown to be brittle in the bend test.

The alloys of greater interest are shown in Table IV. These are the same alloys as were listed in Table II. For these alloys, it is found that the room temperature strength ranges from about 60,000 to slightly over 100,000 pounds per square inch. A few of the alloys are low in ductility and that is generally associated with a composition, such that on aging, or at least in the different tests, the alloys became substantially magnetic. For example, FY became strongly magnetic when aged 24 hours at 1400 degrees Fahr. and tested in tension at room temperature. This alloy does not have sufficient nickel and manganese for an alloy containing 10 per cent of chromium to be stably austenitic. Even with only 6 per cent nickel, as the manganese content increases there is a trend for the elongation value to increase. With alloys containing about 8 per cent of nickel, when the manganese is increased in the range of about 6 to 8 per cent (Alloys FI to FK), the ductility values are quite satisfactory. In the 11 per cent chromium alloys with only 7 per cent nickel, the ductility values were relatively low when the manganese was in the range of 2 to 7 per cent. A combination

of 9 per cent nickel and only 2 per cent manganese gave relatively good ductility. In the 12 per cent chromium alloys, 5 nickel contents were considered, with variations in manganese at each nickel level. The trend is obvious, for the ductility increases with increases in manganese at any nickel level, particularly at the level of about 8 per cent. When the nickel content is increased to 10 per cent, a manganese content of only 3 per cent seems to be adequate.

The strength values of these alloys at 1400 degrees Fahr. range from about 25,000 to over 30,000 pounds per square inch. The higher strength alloys of this group have strengths about equal to the "HH" alloys represented by DX at the same temperature. Thus a survey of the properties of these alloys as listed in Table IV indicates that there is no difficulty in producing alloys of adequate strength at room temperature or at 1400 degrees Fahr. (760 degrees Cent.). On the other hand, the room temperature tests indicate that some limitations must be placed on the alloys to insure the desired ductility.

The relation of composition to ductility is brought out in Fig. 4. The ductility factors (elongation plus reduction of area divided by 2) are plotted as ordinates. The manganese contents are plotted as abscissae. Curves have been drawn in for the nickel levels, 6, 7, 8, and 9 per cent. As indicated, for all nickel levels there is a rather rapid increase in the ductility factor as the manganese increases in the range of about 1 to 3 per cent. The different chromium contents, 10, 11, 12, and 13 per cent, are indicated by special symbols as shown in the legend. For a given chromium content, the ductility increases with the nickel content and also with the manganese content. Various alloys are shown on this graph, and in some cases, their magnetic permeability values are given. Values followed by T mean that the specimen was cut from the threaded portion of the tension test specimen and had, therefore, been subjected to little or no permanent deformation, while values marked R represent specimens for the reduced section of a tension test specimen and, therefore, had considerable cold deformation. It is possible to make use of this graph to select alloy compositions with a range of ductility values when the tests are made on specimens aged 24 hours at 1400 degrees Fahr. (760 degrees Cent.) before testing in tension at room temperature. This chart is to be used in conjunction with Fig. 7, given later, to select alloy compositions with desired characteristics with reference to

**Table IV**

**Summary of Tension Test Data for Alloys of 0.30-0.35% C, 10-13% Cr, 4-10% Ni, 1-10% Mn and 2% Si, Also the Ferro-Magnetic Character of the Nondeformed and Deformed Parts of the Broken Test Bars**

| Alloy No. | Composition, Per Cent Cr | Ni | Mn | Si | C | Tension Test Results for Aged Alloys — Tests at Room Temperature: Tensile Strength Psi. | Yield Strength (0.2% Def.) | Elong. in 2" Per Cent | Red. of Area Per Cent | Tested at 1400° F.: Tensile Strength Psi. | Yield Strength (0.2% Def.) | Elong. in 2" Per Cent | Red. of Area Per Cent | Ferro-Magnetic Character and Permeability Values for Tension Test Specimens Broken — At Room Temp.: Threaded Section | Reduced Section | At 1400° F.: Threaded Section | Reduced Section |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| FY | 10 | 6 | 3 | 2.0 | 0.33 | 60,700 | 41,500 | 5.0 | 1.9 | 26,100 | 19,000 | 15.5 | 15.6 | M | SM (*) | M | W |
| FA | 10 | 6 | 6 | 2.0 | *0.32* | 67,000 | 42,800 | 6.5 | 8.1 | 26,500 | 18,500 | 27.0 | 34.1 | VW (1.03) | M (1.12) | VW | VW |
| FB | 10 | 6 | 7 | 2.0 | 0.33 | 67,500 | 43,600 | 6.0 | 7.0 | 24,700 | 16,800 | 18.5 | 26.8 | N | W | N | N |
| FC | 10 | 6 | 8 | 2.0 | 0.33 | 70,600 | 43,200 | 5.5 | 5.8 | 25,700 | 19,000 | 21.0 | 43.4 | N (1.00) | VW (1.02) | N | N |
| FD | 10 | 6 | 9 | 2.0 | *0.32* | 74,500 | 43,400 | 7.5 | 8.9 | 27,600 | 19,200 | 21.0 | 28.8 | N | VW (1.02) | N | N |
| FE-1 | 10 | 7.0 | 6.1 | 1.96 | 0.32 | 92,300 | 47,400 | 14.0 | 16.0 | 28,200 | 21,400 | 22.0 | 39.8 | N | VW | .. | .. |
| FE | *10.2* | *6.9* | *5.6* | *2.07* | *0.32* | 67,800 | 41,000 | 7.0 | 8.9 | 25,600 | 18,500 | 25.0 | 33.4 | N (1.02) | VW (1.03) | N | N |
| GA | *9.9* | *7.1* | *6.0* | *2.6* | *0.36* | 86,200 | 48,700 | 9.0 | 9.2 | 28,700 | 21,800 | 17.5 | 25.1 | VW (1.00) | W (1.07) | VW | VW |
| FF | 10 | 7 | 7 | 2 | *0.32* | 78,200 | 43,200 | 9.0 | 10.7 | 27,400 | 18,500 | 24.0 | 33.4 | N (1.00) | VW (1.02) | N | N |
| FG | 10 | 7 | 8 | 2 | 0.33 | 78,200 | 44,200 | 11.0 | 11.9 | 26,200 | 18,800 | 20.0 | 33.1 | N | N | N | N |
| GC | 10 | 8 | *3* | *2.16* | *0.33* | 82,800 | 44,400 | 12.5 | 13.0 | 27,000 | 19,300 | 18.5 | 26.1 | VW (1.02) | M (1.20) | W | W |
| FH | *9.5* | *7.6* | *4.6* | *1.92* | *0.32* | 81,500 | 38,800 | 15.5 | 17.9 | ..... | ..... | .... | .... | N (1.01) | W (1.14) | N | N |
| FH-1 | *9.8* | *8.1* | *5.3* | *2.04* | *0.32* | 101,100 | 43,400 | 27.0 | 23.2 | 27,200 | 19,900 | 22.0 | 28.2 | N | VW | .. | .. |
| EJ | 10 | 8 | 5 | 2 | 0.30 | ..... | ..... | .... | .... | 23,400 | 18,500 | 19.0 | 20.9 | .. | .. | N | N |
| FI | *10.3* | *7.8* | *5.7* | *2.16* | *0.33* | 76,200 | 41,200 | 12.0 | 14.8 | 27,100 | 19,300 | 16.0 | 22.0 | N (1.01) | VW (1.02) | N | N |
| FJ | 10 | 8 | 7 | 2 | *0.31* | 83,000 | 45,800 | 12.0 | 14.5 | 28,200 | 19,300 | 28.0 | 37.3 | N | N | N | N |
| FK | 10.1 | *7.9* | *7.6* | *2.13* | *0.33* | 78,400 | 41,800 | 12.0 | 16.1 | 27,500 | ..... | 21.5 | 21.6 | N | N (1.01) | N | N |
| GD | 10 | 9 | 3 | 2 | 0.33 | 78,700 | 40,500 | 15.0 | 20.3 | 27,200 | 19,400 | 24.5 | 29.5 | VW (1.02) | M (1.09) | VW | VW |
| GE | 10 | 9 | 5 | 2 | 0.33 | 88,500 | 40,100 | 21.0 | 20.2 | 26,600 | 19,600 | 21.0 | 26.5 | N | N | N | N |
| GL | 11 | 7 | 2 | 2 | 0.33 | 82,000 | 43,200 | 5.0 | 3.5 | 26,000 | 18,200 | 20.5 | 28.5 | M (1.34) | SM (4.08) | M | M |
| GM | 11 | 7 | 4 | 2 | 0.33 | 83,400 | 47,400 | 8.0 | 7.7 | 26,900 | 19,800 | 25.5 | 33.8 | VW | W | VW | VW |
| FL | 11 | 7 | 6 | 2 | 0.33 | 76,400 | 43,800 | 6.5 | 6.2 | 28,100 | 18,900 | 30.0 | 41.9 | N | VW | N | N |
| FM | 11 | 7 | 7 | 2 | 0.33 | 76,200 | 43,400 | 7.0 | 9.7 | 28,000 | 18,500 | 33.0 | 38.8 | N | VW | N | N |
| GN | 11 | 8 | 1 | 2 | 0.33 | 78,800 | 41,800 | 3.0 | 0.8 | 30,500 | 24,200 | 12.5 | 19.5 | SM (4.12) | SM(*) | M | M |
| GO | 11 | 8 | *2.98* | *2.28* | *0.33* | 78,000 | 45,100 | 8.5 | 13.4 | 26,800 | 20,100 | 14.0 | 24.0 | VW (1.01) | W (1.07) | VW | VW |

**Table IV — (Continued)**

| Alloy No. | Composition, Per Cent Cr | Ni | Mn | Si | C | Tension Test Results for Aged Alloys — Tests at Room Temperature: Tensile Strength Psi. | Yield Strength (0.2% Def.) | Elong. in 2" Per Cent | Red. of Area Per Cent | Tested at 1400° F.: Tensile Strength Psi. | Yield Strength (0.2% Def.) | Elong. in 2" Per Cent | Red. of Area Per Cent | Ferro-Magnetic Character and Permeability Values for Tension Test Specimens Broken — At Room Temp.: Threaded Section | Reduced Section | At 1400° F.: Threaded Section | Reduced Section |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| GP | 11 | 9 | 1 | 2 | 0.33 | 97,600 | 41,200 | 6.0 | 5.0 | 27,000 | 18,400 | 14.5 | 26.8 | SM (2.65) | SM (*) | W | W |
| GQ | 11 | 9 | 2 | 2 | 0.33 | 83,600 | 42,800 | 12.0 | 11.5 | 26,600 | 19,500 | 17.0 | 22.3 | W (1.05) | M (2.16) | VW | N |
| GR | 11 | 10 | 1 | 2 | 0.33 | 104,200 | 42,500 | 13.0 | 3.5 | 27,000 | ..... | 15.5 | 24.8 | M (1.31) | SM (*) | VW | N |
| EO | 12 | 4 | 10 | 2 | 0.30 | ..... | ..... | .... | .... | 27,500 | ..... | 27.5 | 53.3 | .. | .. | N | N (1.00) |
| FN | 12 | 6 | 6 | 2 | 0.33 | 75,100 | 43,800 | 6.0 | 7.7 | 33,000 | 22,000 | 21.0 | 33.8 | VW (1.02) | W (1.09) | N | VW |
| FO | 12 | 6 | 7 | 2 | 0.33 | 79,500 | 45,200 | 6.5 | 7.0 | 28,000 | 22,000 | 19.0 | 30.5 | N (1.01) | W (1.08) | N | N |
| FP | 12 | 6 | 8 | 2 | *0.32* | 76,500 | 43,600 | 6.5 | 7.0 | 27,100 | 18,900 | 26.5 | 37.0 | N | VW (1.01) | N | N |
| FQ | 12 | 6 | 9 | 2 | 0.33 | 83,500 | 44,200 | 10.5 | 11.1 | 29,900 | 20,100 | 14.0 | 16.6 | N (1.01) | VW (1.02) | N | N |
| FR | 12 | 7 | 5 | 2 | 0.33 | 76,200 | 42,500 | 10.0 | 10.7 | 28,200 | 19,000 | 23.5 | 28.2 | N (1.00) | W (1.07) | N | VW |
| FS | 12 | 7 | 6 | 2 | 0.33 | 84,000 | 45,500 | 9.5 | 11.5 | 25,700 | 19,400 | 22.5 | 31.8 | N | W | N | VW |
| FT | 12 | 7 | 8 | 2 | 0.33 | 89,600 | 46,000 | 14.0 | 15.6 | 29,700 | 20,100 | 19.5 | 28.8 | N | N | N | VW |
| GF | 12 | 8 | *3.0* | *2.20* | *0.33* | 85,300 | 41,600 | 15.0 | 12.6 | 30,200 | 20,500 | 24.0 | 22.7 | VW (1.02) | M (1.19) | W | VW |
| FU | 12 | *7.9* | *3.8* | *1.98* | *0.34* | 90,300 | 45,100 | 13.0 | 12.2 | 28,200 | 19,700 | 27.0 | 35.7 | N | W | N | VW |
| FV | 12 | *7.8* | *4.3* | *2.09* | *0.33* | 90,600 | 43,200 | 13.0 | 13.7 | 28,000 | 20,100 | 20.0 | 31.5 | N (1.01) | W (1.07) | N | N |
| FW | 12 | 8 | *5.5* | *2.12* | *0.33* | 90,800 | 46,000 | 20.0 | 18.4 | 31,200 | 19,900 | 26.0 | 38.8 | N | N | N | N |
| FX | *11.4* | *7.9* | *6.7* | *1.77* | *0.32* | 92,700 | 41,800 | 20.0 | 21.6 | 29,800 | ..... | 20.0 | 30.8 | N | VW | N | N |
| GK | *12.3* | *7.8* | *7.8* | *2.28* | *0.35* | 91,200 | 43,100 | 19.0 | 23.4 | 28,000 | 19,500 | 24.5 | 35.7 | N (1.00) | N (1.00) | N | N |
| FX-1 | *11.9* | *8.1* | *8.0* | *2.02* | *0.32* | 98,500 | ..... | 23.0 | 22.3 | 28,400 | 20,700 | 18.0 | 24.1 | N | N | .. | .. |
| GA | 12 | 9 | 3 | 2 | 0.33 | 93,800 | 45,300 | 16.5 | 22.5 | 29,400 | 20,000 | 20.0 | 21.6 | N (1.01) | W (1.11) | VW | VW |
| GG | 12 | 9 | 4 | 2 | 0.33 | 98,100 | ..... | 18.5 | 20.2 | 32,200 | 21,800 | 21.0 | 19.5 | N (1.01) | W (1.055) | N | N |
| GI | 12 | 10 | 3 | 2 | 0.33 | 95,400 | 40,800 | 21.5 | 19.7 | 30,000 | 20,800 | 17.5 | 14.1 | N (1.01) | W (1.09) | N | N |
| GJ | 12 | 10 | 5 | 2 | 0.33 | 93,600 | 42,600 | 19.0 | 18.8 | 32,600 | 21,000 | 14.0 | 18.4 | N (1.01) | N (1.01) | N | N |
| *GB* | *13.1* | *9.0* | *9.2* | *1.59* | *0.24* | *96,500* | *37,800* | *44.0* | *33.8* | *26,300* | *17,200* | *17.5* | *30.8* | *N* | *N* | *N* | *N* |
| GB-A | 13 | 9 | 9 | 1.5 | 0.30 | 101,800 | ..... | 25.0 | 26.5 | 30,200 | 21,600 | 19.0 | 20.9 | N | N | N | N |

NOTE: (1) The composition values in *italic* type are actual amounts as determined by chemical analyses. The other values are intended amounts.

(2) The five degrees of ferro-magnetism and the indicated magnetic permeability values assigned are the following:

N = Non-magnetic, 1.01
W = Weakly, 1.04 to 1.15
SM = Strongly magnetic, =2+
VW = Very weakly, = 1.01 to 1.03
M = Magnetic, 1.15 to 1.40
*Permeability greater than 4.5

ductility, kind of microstructure, and stability of structure. Similarly, these two graphs may be used to give first approximations regarding the properties of any alloy of known composition within the range covered by this research. The results of bend and tension tests are to be supplemented by the results of creep tests and by data on the residual properties of the alloys after the creep tests, as are given in another section of this paper.

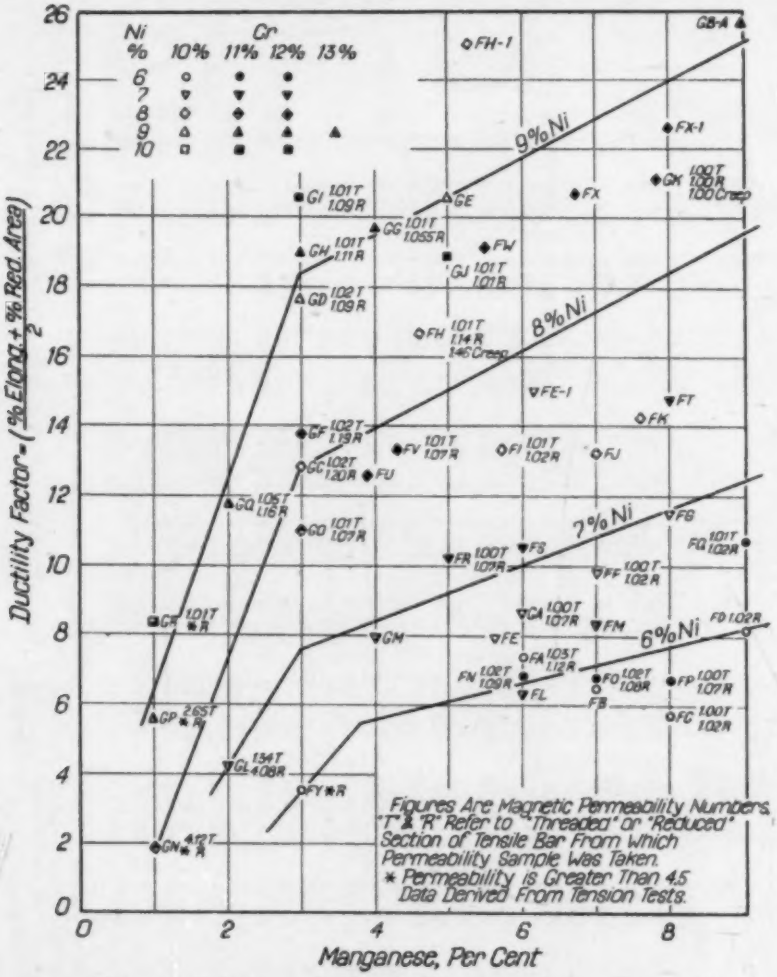


Fig. 4—Relation of Composition to Room Temperature Ductility of Alloys Aged 24 Hours at 1400 Degrees Fahr. Data Derived from Tension Tests.

## Magnetic Properties of the Alloys

The magnetic properties of the alloys have been discussed to some extent in earlier sections, and some data have been given in several of the tables. Magnetic permeability tests give results which

can be correlated with other properties, including microstructures of these alloys.

Comparing the ferro-magnetic character of the alloys fractured at room temperature and those fractured at 1400 degrees Fahr. (760 degrees Cent.), it was noted that in the latter condition, many of the alloys show a decreased degree of ferro-magnetism (See Table IV). This shows, as would be expected from what is known of and published in the literature regarding the iron-chromium-manganese and iron-chromium-nickel systems, that the composition domain of austenite extends to lower nickel or manganese contents at 1400 degrees Fahr. (760 degrees Cent.) than at lower temperatures (1), (2).[2] This placed special interest upon the effects of aging at various temperatures and of deformation at room temperature.

The data in Table V are presented to show further details regarding the relations of composition, aging, and cold deformation to magnetic permeability and, therefore, to the stability of alloys. The permeability values are given for the materials in the following conditions: (A) as aged 24 hours at 1400 degrees Fahr. (760 degrees Cent.), (B) aged and cold-worked, (C) condition B plus 24 hours at 1400 degrees Fahr. (760 degrees Cent.), (D) condition C plus 2 hours at 1800 degrees Fahr. (980 degrees Cent.), (E) condition D plus 2 hours at 2000 degrees Fahr. (1095 degrees Cent.).

The data A and B are for the threaded ends (not deformed) and for the reduced sections (deformed) of tensile test specimens which had been aged 24 hours at 1400 degrees Fahr. (760 degrees Cent.) and then tested in tension. It is evident that specimens, which because of composition were slightly magnetic in the "not-deformed" section, become much more magnetic on cold deformation. For example, GL had a magnetic permeability in the threaded section of only 1.34, while the deformed section showed 4.08. Specimen GP varied from 2.64 to more than 4.5, GQ from 1.05 to 2.15, and GR from 1.31 to over 4.5. These alloys were all deficient in nickel and/or manganese. Some of the alloys showed no difference in these two sections, and obviously that means that they contained sufficient austenitizing metals to make them stable in these tests.

For these slightly unstable alloys, aging the deformed specimen

[2]The figures appearing in parentheses pertain to the bibliography appended to this paper.

**Table V**

**The Magnetic Permeability of Aged and Cold Deformed Materials. Specimens Prepared From Broken Tension Test Bars of Aged Alloys**

| Alloy No. | Composition, Per Cent | | | | | (A) Threaded Section of Bar Not Deformed | (B) Reduced Section of Bar Deformed | As in (B) plus: (1) | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Cr | Ni | Mn | Si | C | | | 24 Hrs. at 1400 °F. | 2 Hrs. at 1800 °F. | 2 Hrs. at 2000 °F. |
| FY | 10 | 6 | 3 | 2 | 0.33 | .... | * | * | .... | ..... |
| FA | 10 | 6 | 6 | 2 | 0.33 | 1.03 | 1.12 | 2.34 | .... | ..... |
| FN | 12 | 6 | 6 | 2 | 0.33 | 1.02 | 1.09 | 1.00 | .... | ..... |
| FO | 12 | 6 | 7 | 2 | 0.33 | 1.02 | 1.08 | 1.01 | .... | ..... |
| FC | 10 | 6 | 8 | 2 | 0.33 | 1.00 | 1.02 | 1.02 | .... | ..... |
| FP | 12 | 6 | 8 | 2 | 0.32 | .... | 1.01 | 1.01 | .... | ..... |
| FD | 10 | 6 | 9 | 2 | 0.33 | ... | 1.02 | 1.02 | .... | ..... |
| FQ | 12 | 6 | 9 | 2 | 0.33 | 1.01 | 1.02 | 1.01 | .... | ..... |
| GL | 11 | 7 | 2 | 2 | 0.33 | 1.34 | 4.08 | * | .... | ..... |
| FR | 12 | 7 | 5 | 2 | 0.33 | 1.00 | 1.07 | 1.01 | .... | ..... |
| FE | 10.2 | 6.9 | 5.6 | 2.04 | 0.32 | 1.02 | 1.03 | 1.02 | 1.02 | 1.015 |
| GA | 9.9 | 7.1 | 6.0 | 2.6 | 0.36 | 1.00 | 1.07 | 1.02 | .... | ..... |
| FF | 10 | 7 | 7 | 2 | 0.32 | 1.00 | 1.02 | 1.02 | .... | ..... |
| GN | 11 | 8 | 1 | 2 | 0.33 | 4.12 | * | * | .... | ..... |
| GC | 10 | 8 | 3 | 2 | 0.33 | 1.02 | 1.20 | 3.60 | .... | ..... |
| GO | 11 | 8 | 2.98 | 2.28 | 0.33 | 1.01 | 1.07 | 1.12 | 1.05 | 1.02 |
| GF | 12 | 8 | 3 | 2 | 0.33 | 1.02 | 1.19 | 1.20 | 1.03 | 1.02 |
| FH | 9.5 | 7.6 | 4.6 | 1.92 | 0.32 | 1.01 | 1.14 | 1.06 | 1.02 | 1.02 |
| FV | 12 | 7.8 | 4.3 | 2.09 | 0.33 | 1.02 | 1.07 | 1.00 | 1.02 | 1.015 |
| FI | 10 | 8 | 6 | 2 | 0.32 | 1.01 | 1.02 | 1.00 | 1.02 | 1.02 |
| FW | 12 | 8 | 5.5 | 2.12 | 0.33 | .... | 1.01 | .... | .... | ..... |
| FK | 10 | 8 | 8 | 2 | 0.33 | .... | 1.01 | 1.02 | .... | ..... |
| GK | 12.3 | 7.8 | 7.8 | 2.28 | 0.35 | 1.00 | 1.00 | 1.02 | .... | ..... |
| GP | 11 | 9 | 1 | 2 | 0.33 | 2.64 | * | * | .... | ..... |
| GQ | 10 | 9 | 3 | 2 | 0.33 | 1.05 | 2.15 | 2.60 | 1.02 | 1.02 |
| GD | 10 | 9 | 3 | 2 | 0.33 | 1.02 | 1.07 | 1.32 | 1.02 | 1.01 |
| GH | 12 | 9 | 3 | 2 | 0.33 | 1.01 | 1.11 | 1.02 | 1.02 | 1.005 |
| GG | 12 | 9 | 4 | 2 | 0.33 | 1.01 | 1.06 | 1.03 | 1.02 | 1.02 |
| GR | 11 | 10 | 1 | 2 | 0.33 | 1.31 | * | * | .... | ..... |
| GI | 12 | 10 | 3 | 2 | 0.33 | 1.02 | 1.10 | 1.01 | 1.02 | 1.02 |
| GJ | 12 | 10 | 5 | 2 | 0.33 | 1.00 | 1.01 | 1.01 | 1.01 | 1.005 |

NOTE: An asterisk (*) means a permeability greater than 4.5.
(1) The permeability specimens were quenched in water from the annealing temperatures.

(B) for 24 hours at 1400 degrees Fahr. (760 degrees Cent.) caused further transformation. For example, this treatment increased the magnetic permeability of FA from 1.12 to 2.34, GC from 1.20 to 3.60, and GD from 1.07 to 1.32.

On the other hand, heating 2 hours at 1800 or 2000 degrees Fahr. (980 or 1095 degrees Cent.) and quenching removed the effects of cold-work transformation and reduced the magnetic permeability to a value corresponding about to that of the non-deformed section.

From these limited tests, it is again shown that the composition boundary of the austenitic alloys shifts to lower nickel and/or manganese contents with increasing temperature, or stated another way, when these alloys are austenitic after aging at 1400 degrees Fahr. (760 degrees Cent.), they are also austenitic on heating at 1800 or 2000 degrees Fahr. (980 or 1095 degrees Cent.). A more detailed study will be needed if it is desired to more accurately establish the phase boundaries as a function of temperature, however.

## Relation of Composition to Structure, Stability, and Properties of Alloys

It is evident from the data already available that the structures of the alloys, the stability of the structures, and the properties of the alloys depend upon the composition, more particularly the relation of the chromium content to the nickel and/or manganese contents. It has already been pointed out that, depending upon variation in composition, these alloys may be wholly austenitic as-cast and after aging for 24 hours at 1400 degrees Fahr. (760 degrees Cent.), or they may be slightly magnetic as-cast and become more magnetic on aging. It has also been pointed out that alloys which remain wholly austenitic under these conditions may be transformed more or less under the influence of cold deformation as in the tension test at room temperature.

Data have been presented for certain relations which have been found with reference to the influence of composition on the ductility as shown in Fig. 4. It is now proposed to present a general picture of the relation of composition to structure, stability, and properties of alloys containing carbon in the range of about 0.30 to 0.35 per cent and about 2 per cent silicon, with chromium in the range of about 10 to 13 per cent, nickel in the range of 4 to 10 per cent, but more particularly in the range of 6 to 9 per cent,

and manganese in the range of 1 to 12 per cent, but more particularly in the range of 2 to 10 per cent. This information is shown in Fig. 7 and is intended to represent alloys aged 24 hours at 1400 degrees Fahr. (760 degrees Cent.). Other conditions of aging and deforming will be covered in the discussion.

As an aid in presenting this diagram, which is essentially for alloys of chromium-nickel-manganese-iron, some consideration has been given to publications dealing with the somewhat simpler systems of chromium-nickel-iron and chromium-manganese-iron.

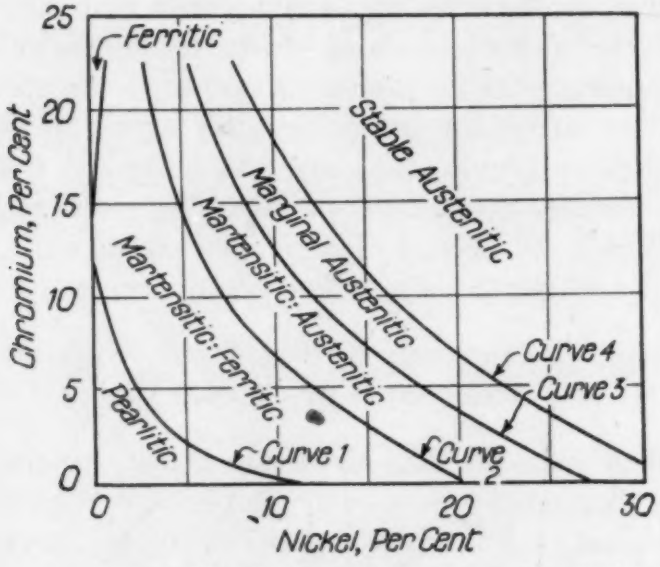


Fig. 5—Constitutional Diagram of Low-Carbon Iron-Chromium-Nickel Alloys.

*Chromium-Nickel-Iron System* — This system has been studied by numerous investigators, but the work which seems to be most pertinent to the present study is that by Pilling (1). His Fig. 2 is reproduced as Fig. 5. The special interest is in alloys containing 10 to 15 per cent chromium. His diagram is for low-carbon alloys generally less than 0.1 per cent and is, therefore, not strictly applicable to the present alloys. His curves, however, do serve to show the relation of chromium and nickel to stable austenitic alloys and to marginal alloys, and that as the chromium content is decreased, the nickel must be increased as shown by his Curve 4. For example, with a chromium content of 15 per cent, the nickel may be only of the order of 12 per cent, but when the chromium content is decreased to 10 per cent, the nickel content must be increased to 16 per cent or more. His Curve 3 gives the boundary for marginal austenitic alloys, and this region is comparable to certain

regions discussed in the present alloys in Fig. 7. His diagram further shows that as the nickel and chromium contents are decreased, alloys which are partly martensitic and partly austenitic are encountered, and on further decrease in chromium and nickel, the alloys finally become martensitic and ferritic. It is to be expected that the alloys in the present study which are higher in nickel than in manganese will behave more like the diagram shown by Pilling, and this is the general character of the curves for 9 and 8 per cent nickel as shown in Fig. 7. But as the nickel is decreased to 6 per cent, the curve takes on more of the shape of the boundary for the austenite field in the chromium-manganese-iron system. (See Fig. 6.)

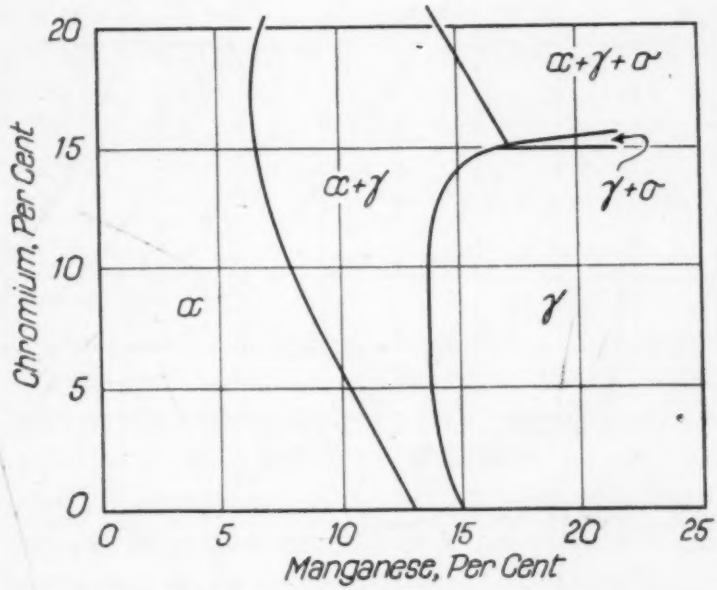


Fig. 6—Constitution of Alloys Slow Cooled from 1000 Degrees Cent. (1832 Degrees Fahr.)

*Chromium-Manganese-Iron System* — This system has been studied by Burgess and Forgeng (2), and the data shown in their Fig. 7 have been used to construct Fig. 6. This represents the constituents of alloys slowly cooled from 1830 degrees Fahr. (1000 degrees Cent.) and is shown primarily to represent the relation of chromium and manganese to the structures obtained. We are particularly interested in the chromium contents between 10 and 15 per cent. At 10 per cent chromium, the ferritic field is represented to extend to a manganese content of about 7.5 per cent. There is a heterogeneous field of ferrite plus austenite at this chromium content until the manganese is increased to about 13.5

per cent. At 12.5 per cent of chromium the heterogeneous field (alpha plus gamma) is widened in both directions, and this trend is also found at 15 per cent chromium. According to this diagram, when the chromium content is above 15 per cent, increasing the manganese content will not produce the austenitic structure. This diagram is of interest only in that it shows the trend for this system and how it might influence our alloys which are relatively

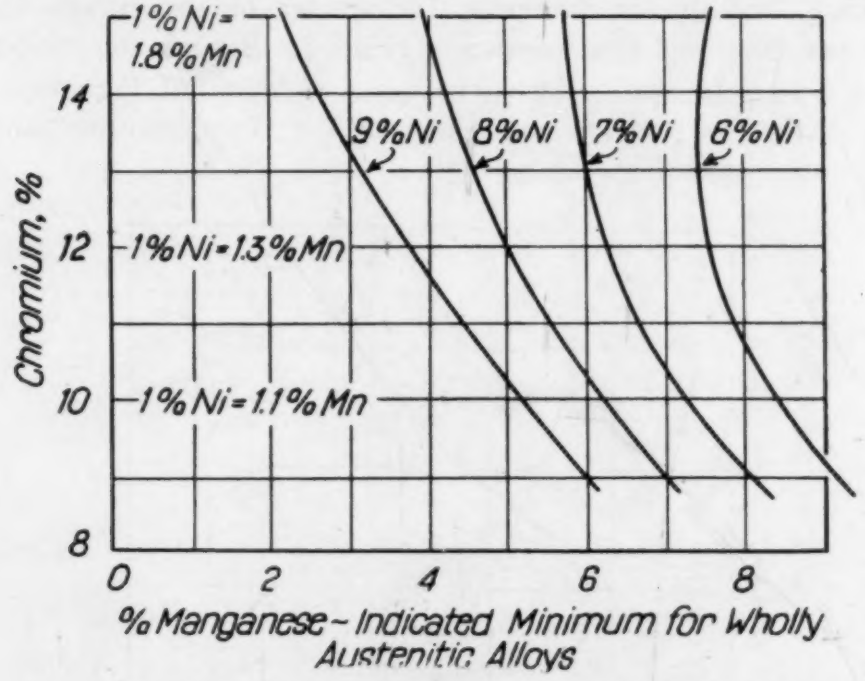


Fig. 7—Relation of Chromium, Nickel and Manganese Contents to Structures of Alloys Containing About 0.30 to 0.35 Per Cent Carbon and About 2.00 Per Cent Silicon. Alloys Aged 24 Hours at 1400 Degrees Fahr. and Cold-Deformed.

I. (a) Alloys to the right of the curves for the various nickel levels are designated wholly austenitic, that is, they are nonmagnetic as cast, after aging 24 hours at 1400 degrees Fahr., and after cold deformation as in the tension test.

(b) Alloys only slightly to the right of the curves for the various nickel levels may transform and become more or less magnetic on cold deformation following extended aging at elevated temperatures, such as 500 hours at 1200 degrees Fahr.

(c) The minimum nickel contents for the more truly stable wholly austenitic alloys are about 1 per cent greater than that indicated in the figure for the various nickel levels, or about the manganese equivalent of 1 per cent nickel higher in manganese than indicated in the graph.

II. Alloys to the left of the curves for the various nickel levels are considered marginal austenitic alloys with manganese deficiencies up to as much as 2 to 3 per cent. Such alloys are nonmagnetic as cast and after aging 24 hours at 1400 degrees Fahr. but transform and become more or less magnetic on cold deformation. The amount of transformation and attendant loss of ductility increase as the alloy compositions are removed to the left from the curves on the graph. Lack of stability of the austenite is most evident on long-time aging followed by cold working.

III. Alloys farther to the left than the marginal austenitic compositions described under II may show marked transformation on aging or be partially to wholly martensitic or ferritic in the as-cast condition

high in manganese. Thus the alloys in which manganese is substantially in excess of the nickel may be expected to behave more like the chromium-manganese-iron alloys, and similarly, alloys which are higher in nickel than in manganese may be expected to behave more like the chromium-nickel-iron alloys discussed above.

*Relation of Chromium, Nickel, and Manganese Content to Structures of Emergency Heat Resistant Alloys* — Fig. 7 represents the relations between composition and structural characteristics which have been found in studying alloys containing chromium mostly in the range of 10 to 15 per cent, nickel in the range of about 4 to 10 per cent, and manganese in the range of about 1 to 12 per cent. This diagram has been drawn to represent the structures and the stabilities of alloys aged 24 hours at 1400 degrees Fahr. (760 degrees Cent.) and cold-deformed as in tension testing after aging. This basis of classification was adopted because it was the only condition in which practically all of the alloys had been tested and for which extensive data were available. The ordinates are chromium and manganese, and the curves for nickel levels of 9, 8, 7, and 6 per cent have been drawn in. For chromium levels of 15, 12, and 10, approximate manganese equivalents for nickel have been indicated.

Frequent references are made to this diagram. It is to be emphasized that the diagram is for alloys containing carbon in the range of 0.30 to 0.35 per cent and about 2 per cent silicon, and that it is for alloys aged 24 hours at 1400 degrees Fahr. (760 degrees Cent.) and cold-deformed in tension testing after aging. Consideration may be given to alloys containing 9 per cent of nickel, and it is shown that for 15 per cent of chromium, the manganese required for the wholly austenitic structure is about 2.2 per cent. The expression "wholly austenitic" is used to represent alloys which do not transform or become magnetic under the conditions stated above. If the chromium content is decreased to 10 per cent, the manganese content must be increased to about 5 per cent in order to produce a wholly austenitic alloy. Similar relations are indicated by Fig. 7 for nickel contents of 8, 7, and 6 per cent.

As indicated earlier, alloys falling within certain limits to the left of the curves for the various nickel levels are marginal alloys. That is, under some conditions they are not stably austenitic. If the manganese content in any given alloy is of the order of 2 to 3

per cent below the indicated values in Fig. 7, the alloys transform to some extent on aging at 1400 degrees Fahr. (760 degrees Cent.) and become more or less magnetic. The 2 per cent manganese deficiency mentioned above seems to apply to the higher chromium-lower manganese alloy and 3 per cent to the lower chromium-higher manganese alloys. When this deficiency in manganese is greater than 2 to 3 per cent, the alloys become more or less martensitic on aging and in extreme cases may become quite low in ductility on aging and may even be magnetic as cast.

Alloys which are only slightly to the left of the curves in Fig. 7, or in other words, deficient in manganese, not over ½ to 1 per cent, are austenitic and nonmagnetic as cast and after aging 24 hours at 1400 degrees Fahr. (760 degrees Cent.) but may transform somewhat on cold deformation as when fractured in a tension test. Long-time aging, for example, 500 hours at 1200 degrees Fahr., may also cause some transformation, and the lack of stability is most evident from the increased ferro-magnetism induced by cold deformation following long-time aging.

Alloys to the right of the curves for the different nickel levels in Fig. 7 are designated as wholly austenitic, but this means only that they are wholly austenitic as-cast and after aging for 24 hours at 1400 degrees Fahr. (760 degrees Cent.) and on cold deformation after aging. Some of these alloys which are only slightly to the right of curves may, however, transform somewhat under the influence of cold working if the alloy has been aged for an extended period of time, for example, 500 hours at 1200 degrees Fahr. (650 degrees Cent.) prior to cold deformation. It is, therefore, evident that in order to have alloys which are stable under the combined conditions of long-time aging and cold deformation, the composition must be substantially to the right of the curves shown in Fig. 7. Alloy GK meets this specification. With a chromium content of 12.3 per cent and 7.8 per cent nickel, the indicated amount of manganese is about 5.2 per cent, whereas this alloy contains 7.8 per cent. Alloy GK is nonmagnetic even after aging for 500 hours at 1200 degrees Fahr. (650 degrees Cent.) and pulling in tension. Thus, if it is desired to have an alloy which is sufficiently stable that there is no transformation even on prolonged aging followed by cold working, it seems that the nickel should be increased about 1 per cent above the values shown in Fig. 7, or that the manganese should be increased about the

equivalent of 1 per cent nickel. The manganese equivalents for nickel at different chromium levels are shown in Fig. 7.

It is not intended to state or to imply that alloys only slightly to the right of the curves in Fig. 7, which remain wholly austenitic on aging 24 hours at 1400 degrees Fahr. (760 degrees Cent.) but which may transform somewhat on long-time aging followed by cold working, are not usable in engineering applications. Extensive tests have shown that such alloys have rather good ductility values even after aging for 500 hours at 1200 degrees Fahr. (650 degrees Cent.). Data on this point are given in a later section. Possibly in some special applications where there would be severe cold working, troublesome loss in ductility might be encountered.

Furthermore, alloys which are in the marginal field by as much as about 0.5 to 1 per cent manganese less than indicated by the curve for wholly austenitic alloys have been found to have rather good retained ductility values after aging for as long as 500 hours at 1200 degrees Fahr. (650 degrees Cent.). However, if the alloys depart too much from the composition indicated as wholly austenitic, then excessive loss of ductility can be encountered.

As shown in Table IV, Alloys FY, GL, and GN showed low ductilities in the tension test after aging 24 hours at 1400 degrees Fahr. (760 degrees Cent.). From Fig. 7, it is indicated that Alloy FY should have about 8.5 per cent manganese to be wholly austenitic, and it had only 3 per cent. Alloy GL needed 6 to 7 per cent manganese, but had only 2 per cent. Similarly, Alloy GN needed 5 to 6 per cent manganese, but had only 1 per cent. After aging 24 hours at 1400 degrees Fahr. (760 degrees Cent.), these alloys show ductility factors of 3.5, 4.2, and 1.9 in the order discussed. All of these alloys become magnetic on aging.

Alloy GQ retained rather good ductility on aging 24 hours at 1400 degrees Fahr. (750 degrees Cent.), but on aging 500 hours at 1200 degrees Fahr. (650 degrees Cent.), its ductility factor was only 2.5. See Table VIII. Comparing the composition of Alloy GQ with Fig. 7, it needed 4 to 5 per cent of manganese to produce the wholly austenitic structure, but had only 2 per cent, or a deficiency of 2 to 3 per cent manganese.

These illustrations are intended to show the manner in which Fig. 7 can be used to give first approximations of the structures, the stability of structures, and the ductility of alloys under various conditions of exposure to elevated temperatures.

In the discussion under creep tests it is pointed out that the wholly austenitic alloys, as indicated by Fig. 7, have substantially higher load-carrying capacities at 1400 and 1600 degrees Fahr. (760 and 870 degrees Cent.) than the alloys which are only marginally austenitic and which transform on heating to the creep testing temperature or during the creep test.

The diagram of Fig. 7 has been drawn for alloys containing carbon in the range of 0.30 to 0.35 per cent. From the limited amount of work on the effect of carbon, it is indicated that carbon has relatively small effects on stability and structures. Certainly it does not have the pronounced effect noted in alloys of the "HH" type by Gow and Harder (4). A very limited amount of work has been done on nitrogen, and no definite statement can be made with reference to its effect on the curves in Fig. 7.

## Properties of Alloys at Intermediate Temperatures and the Effect of Aging at Intermediate Temperatures

The discussion of the previous sections has dealt with the room temperature properties of alloys after aging at 1400 degrees Fahr. (760 degrees Cent.) and the properties of alloys at elevated temperatures of 1400 degrees Fahr. (760 degrees Cent.). The results of such tests form the basis for the diagram shown in Fig. 7.

However, the contemplated uses for these alloys would involve service at intermediate temperatures such as 1000 to 1200 degrees Fahr. (540 to 650 degrees Cent.), and it was considered necessary to determine the effects of heating at these temperatures on the resulting properties of the alloys and the properties of the alloys at intermediate temperatures. For example, would the alloys be embrittled by heating at 1000 to 1200 degrees Fahr. (540 to 650 degrees Cent.), or would they be brittle or weak at these temperatures? Selected alloys were aged at these intermediate temperatures for 24 and for 500 hours and used for bend and tension tests. Some attention was also given to microstructures and to magnetic permeability. Alloy GK was tested in tension at room temperature after aging at intermediate temperatures and was also tested in tension at intermediate temperatures.

*Bend and Tension Test Results for Alloys Aged at Temperatures from 1000 to 1600 Degrees Fahr. for 24 Hours*—Bend tests were made on strip castings of three compositions, as shown in

**Table VI**
**Bend Test Results for Alloys Aged at Temperatures of 1000 to 1600 Degrees Fahr.**

| Alloy No. | Composition—Per Cent* Cr | Ni | Mn | Si | C | Bend Test Results—Alloys Aged 24 Hours at Temperatures Shown Degrees Fahr. |
|---|---|---|---|---|---|---|
| FE-2 | 10 | 7 | 5.63 | 2 | 0.34 | 1000—Full Bend—No tearing |
| | | | | | | 1100—Full Bend—Few tears at center |
| | | | | | | 1200—Full Bend—No tearing |
| | | | | | | 1300—Full Bend—No tearing |
| | | | | | | 1400—Full Bend—No tearing |
| | | | | | | 1600—Full Bend—Few tears at center |
| FH-2 | 10 | 8 | 4.65 | 2 | 0.29 | 1000—Full Bend—No tearing |
| | | | | | | 1100—Full Bend—No tearing |
| | | | | | | 1200—Full Bend—Few tears at center |
| | | | | | | 1300—Full Bend—Few tears at center |
| | | | | | | 1400—Full Bend—Few tears at center |
| | | | | | | 1600—Full Bend—No tearing |
| GK-2 | 12 | 8 | 6.80 | 2 | 0.33 | 1000—Full Bend—No tearing |
| | | | | | | 1100—Full Bend—No tearing |
| | | | | | | 1200—Full Bend—Few tears at center |
| | | | | | | 1300—Broke—105-Degree Bend |
| | | | | | | 1400—Full Bend—Tearing at center |
| | | | | | | 1600—Full Bend—No tearing |

*The strip castings used in this work were produced by remelting heads and runners from earlier made castings of these compositions. The manganese and carbon contents shown are the actual amounts as determined by chemical analyses. The chromium, nickel and silicon contents shown are intended amounts.

Table VI, after aging the materials for 24 hours at temperatures of 1000, 1100, 1200, 1300, 1400, and 1600 degrees Fahr. (540, 595, 650, 705, 760 and 870 degrees Cent.). This was to determine whether some other temperature might show a greater loss of ductility for the alloys than the 1400 degrees Fahr. treatment that had been employed.

The alloys which were used in these bend tests represented two materials (FE-2 and FH-2) which were known to be slightly ferritic and one (GK) which had been found to be wholly austenitic under all previous conditions of testing. While all of the specimens, except one of GK, aged at 1300 degrees Fahr. (705 degrees Cent.), took a full bend after all of the aging treatments, there is some indication of loss of ductility on aging at 1200 to 1300 degrees Fahr. (650 to 705 degrees Cent.).

Alloy GK has been tested in tension at room temperature while in the "as-cast" condition and after aging 24 hours at 1000, 1200, 1400, and 1600 degrees Fahr. (540, 650, 760 and 870 degrees Cent.). Elevated temperature tension tests have also been made at 1000, 1200, 1400, and 1600 degrees Fahr. (540, 650, 760 and 870 degrees Cent.). These results are given in Table VII.

The room temperature tensile strength is higher for the

**Table VII**
**The Tensile Properties of Alloy GK**

A—At room temperature for "as-cast" and "aged" alloys.
B—At elevated temperatures for pre-aged material.

| Alloy No. | | Tensile Strength Psi. | Yield Strength (0.2 Per Cent Def.) | Elongation in 2 Inches Per Cent | Reduction of Area Per Cent |
|---|---|---|---|---|---|
| | A—Room Temperature Tension Tests on "Aged" Material | | | | |
| Aged 24 Hours at: | | | | | |
| GK | As cast | 78,400 | 40,200 | 32.0 | 23.7 |
| GK | 1000 Degrees Fahr. | 74,700 | 40,000 | 31.5 | 33.8 |
| GK | 1200 Degrees Fahr. | 77,800 | 43,100 | 20.0 | 29.7 |
| GK | 1400 Degrees Fahr. | 91,200 | 43,100 | 19.0 | 23.4 |
| GK | 1600 Degrees Fahr. | 88,500 | 36,800 | 14.5 | 12.6 |
| | B—Elevated Temperature Tension Tests of "Aged" Material | | | | |
| | Temp. of Test | | | | |
| GK | 1000 Degrees Fahr. | 60,600 | 22,400 | 33.5 | 37.3 |
| GK | 1200 Degrees Fahr. | 46,600 | 21,700 | 16.5 | 22.7 |
| GK | 1400 Degrees Fahr. | 28,000 | 19,500 | 24.5 | 35.7 |
| GK | 1600 Degrees Fahr. | 12,400 | 10,700 | 31.0 | 40.1 |

*Alloy material pre-aged 24 hours at the temperatures at which the tension tests were conducted.

| Alloy Compositions | | | | | |
|---|---|---|---|---|---|
| Alloy No. | Cr | Ni | Mn | Si | C |
| GK | 12.3 | 7.8 | 7.8 | 2.28 | 0.35 |

specimens aged at 1400 and 1600 degrees Fahr. (760 and 870 degrees Cent.) than for the specimens "as-cast" or aged at 1000 and 1200 degrees Fahr. (540 and 650 degrees Cent.). The lowest ductility (14.5 per cent elongation) is shown for the specimen aged at 1600 degrees Fahr. (870 degrees Cent.). The elevated temperature tension tests show a drop in strength properties with increased temperatures from 1000 to 1600 degrees Fahr. (540 to 870 degrees Cent.) with the most marked percentage drop occurring in going from 1400 to 1600 degrees Fahr. (760 to 870 degrees Cent.). However, the ductility does not vary directly with temperature but shows a distinct minimum at 1200 degrees Fahr. (650 degrees Cent.). It thus appeared that the lowest ductility of Alloy GK was developed by aging at 1200 degrees Fahr. (650 degrees Cent.), and further tests were made to determine the effect of longer aging time at this temperature, using a series of eleven alloys. Comparisons are made between these results and those obtained on aging at 1400 degrees Fahr. (760 degrees Cent.).

## Long-Time Aging Tests at 1200 Degrees Fahr.

It has been considered of special importance to determine the relative permanence of these alloys over the whole possible range of operating temperatures, and the results just discussed indicated

the importance of tests at 1200 degrees Fahr. (650 degrees Cent.). Studies have, therefore, been made on the effects of aging 24 hours at 1400 degrees Fahr. (760 degrees Cent.) and 500 hours at 1200 degrees Fahr. (650 degrees Cent.) on the tensile properties and the magnetic properties of representative alloys. A temperature of 1400 degrees Fahr. (760 degrees Cent.) is of interest because it is the contemplated service temperature, and the temperature of 1200 degrees Fahr. (650 degrees Cent.) is of special interest because it was found that 1200 degrees Fahr. (650 degrees Cent.) is probably the most severe temperature for retention of adequate ductility, or stated another way, the temperature at which aging produced maximum losses in ductility. The magnetic permeability tests are of interest because of the correlation between transformation and the mechanical properties and also for the purpose of correlating these two properties with the composition of the alloy.

*Effect of Aging on the Tensile Properties* — Results of tension tests on specimens aged 24 hours at 1400 degrees Fahr. (760 degrees Cent.) and 500 hours at 1200 degrees Fahr. (650 degrees Cent.) are shown in Table VIII. In addition to the alloys with chromium in the range of about 10 to 12 per cent, Alloy DU, representative of the 18-8 type, has been included. The tensile strengths in the aged condition of 24 hours at 1400 degrees Fahr. (760 degrees Cent.) range from 81,000 to 98,000 pounds per square inch, and the 18-8 alloy falls within this range. The yield strength values varied over a comparatively narrow range such as 38,800 to 49,900 pounds per square inch for 0.2 per cent deformation. Again the properties for the 18-8 alloy are within these ranges. Elongation values range from 10.5 to 19.0 for the emergency alloys as compared with 25.5 for "18-8". Reduction of area values range from 11.1 to 23.4 for the emergency alloys compared to 20.6 for the 18-8 alloy. Thus there are no startling properties found for the aged specimens. To be sure there are some variations in strength and in ductility. It can probably be assumed that the strengths and the ductilities of these alloys would all be acceptable.

In the case of the alloys aged 500 hours at 1200 degrees Fahr. (650 degrees Cent.), one alloy, GQ, developed low ductility values of 3.0 per cent elongation and 1.9 per cent reduction of area. Examination of Fig. 7 shows that for the chromium-nickel content

**Table VIII**

**Room Temperature Tension Test Results for Alloy Materials Aged 24 Hours at 1400 Degrees Fahr. and 500 Hours at 1200 Degrees Fahr.**

| | Alloy No. | FQ | FE-1 | FH | FV | GK | GK-2* | GQ | GH | GG | GT | DU |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Material Aged 24 Hours at 1400 Degrees Fahr. | C | 0.33 | 0.32 | 0.32 | 0.33 | 0.35 | 0.32 | 0.33 | 0.33 | 0.33 | 0.33 | 0.30 |
| | Cr | 12 | 10 | 9.5 | 12 | 12.3 | 12 | 11 | 12 | 12 | 12 | 18 |
| | Ni | 6 | 7 | 7.6 | 7.8 | 7.8 | 8 | 9 | 9 | 9 | 9 | 8 |
| | Mn | 9 | 6.1 | 4.6 | 4.3 | 7.8 | 8 | 2 | 3 | 4 | 9 | 1 |
| | Si | 2 | 1.96 | 1.92 | 2.09 | 2.28 | 2 | 2 | 2 | 2 | 2 | 1 |
| Tensile Strength, psi. | | 83,500 | 92,300 | 81,000 | 90,600 | 91,200 | 94,000 | 83,600 | 93,800 | 98,100 | 93,200 | 97,100 |
| Yield Strength (0.2 Per Cent Def.), psi. | | 44,200 | 47,400 | 38,800 | 44,200 | 43,100 | 49,900 | 42,800 | 45,300 | .... | 46,500 | 45,000 |
| Elongation in 2 Inches, Per Cent | | 10.5 | 14.0 | 15.5 | 13.0 | 19.0 | 10.5 | 12.0 | 16.5 | 18.5 | 13.5 | 25.5 |
| Reduction of Area | | 11.1 | 16.0 | 17.9 | 13.7 | 23.4 | 13.3 | 11.5 | 22.5 | 20.2 | 18.8 | 20.6 |
| | Alloy No. | FQ-2 | FE-1 | FH-2 | FV-2 | GK | GK-2* | GQ | GH-2 | GS | GT | DU-2 |
| Material Aged 500 Hours at 1200 Degrees Fahr. | C | 0.33 | 0.32 | 0.32 | 0.32 | 0.35 | 0.32 | 0.33 | 0.32 | 0.32 | 0.32 | 0.32 |
| | Cr | 12 | 10 | 10 | 12 | 12.3 | 12 | 11 | 12 | 12 | 12 | 18 |
| | Ni | 6 | 7 | 8 | 8 | 7.8 | 8 | 9 | 9 | 9 | 9 | 8 |
| | Mn | 9 | 6.1 | 5 | 5 | 7.8 | 8 | 2 | 3 | 5 | 9 | 1 |
| | Si | 2 | 1.96 | 2 | 2 | 2.28 | 2 | 2 | 2 | 2 | 2 | 1 |
| Tensile Strength, psi. | | 89,400 | 99,000 | 82,900 | 87,100 | 93,600 | 105,000 | 126,200 | 116,000 | 98,600 | 103,000 | 109,000 |
| Yield Strength (0.2 Per Cent Def.), psi. | | 44,200 | 48,000 | 42,000 | 47,000 | 41,800 | 50,200 | 51,500 | 42,100 | 45,000 | 45,300 | 45,500 |
| Elongation in 2 Inches, Per Cent | | 7.5 | 11.0 | 8.0 | 7.0 | 10.5 | 12.0 | 3.0 | 12.5 | 14.0 | 13.5 | 17.0 |
| Reduction of Area, Per Cent | | 9.7 | 10.0 | 6.3 | 7.7 | 14.8 | 14.5 | 1.9 | 11.5 | 16.3 | .... | 17.0 |

*Nitrogen intended 0.10 per cent.

for this alloy, it should contain at least 4.4 per cent manganese to make it a stable austenite, whereas the alloy contains only 2 per cent manganese. This means that this alloy is so far out of balance in composition that it transforms extensively on aging at this temperature. The data in Table IX show that both the reduced section and the nondeformed section of the tension test specimen had magnetic permeability values in excess of those determinable

**Table IX**

**The Magnetic Permeability of Aged and Cold Deformed Materials**

(Specimens prepared from broken tension test bars of alloy materials which had been aged 24 hours at 1400 degrees Fahr. and 500 hours at 1200 degrees Fahr.

| Alloy No. | Composition, Per Cent | | | | | Aged 24 Hours at 1400 Degrees Fahr. Section of Bar | | Aged 500 Hours at 1200 Degrees Fahr. Section of Tensile Bar | |
|---|---|---|---|---|---|---|---|---|---|
| | C | Cr | Ni | Mn | Si | "Threaded" Not Deformed | "Reduced" Deformed | "Threaded" Not Deformed | "Reduced" Deformed |
| FQ | 0.33 | 12 | 6 | 9 | 2 | 1.01 | 1.02 | .... | .... |
| FQ-2 | 0.32 | 12 | 6 | 9 | 2 | .... | .... | 1.01 | 1.14 |
| FE-1 | 0.32 | 10 | 7 | 6.1 | 1.96 | N* | VW* | 1.06 | 1.60 |
| FH | 0.32 | 9.5 | 7.6 | 4.6 | 1.92 | 1.01 | 1.14 | .... | .... |
| FH-2 | 0.32 | 10 | 8 | 5 | 2 | .... | .... | 1.04 | 2.63 |
| FV | 0.33 | 12.0 | 7.8 | 4.3 | 2.09 | 1.02 | 1.07 | .... | .... |
| FV-2 | 0.32 | 12 | 8 | 5 | 2 | .... | .... | 1.035 | 1.26 |
| GK | 0.35 | 12.3 | 7.8 | 7.8 | 2.28 | 1.00 | 1.00 | 1.00 | 1.00 |
| GK-2 | 0.32 | 12 | 8 | 8 | 2 | .... | .... | 1.01 | 1.03 |
| GQ | 0.33 | 11 | 9 | 2 | 2 | 1.05 | 2.15 | 4.+ | 4.+ |
| GH | 0.33 | 12 | 9 | 3 | 2 | 1.01 | 1.11 | .... | .... |
| GH-2 | 0.32 | 12 | 9 | 3 | 2 | .... | .... | 1.475 | 4.+ |
| GG | 0.33 | 12 | 9 | 4 | 2 | 1.01 | 1.06 | .... | .... |
| GS | 0.33 | 12 | 9 | 5 | 2 | N* | N* | 1.035 | 1.340 |
| GT | 0.33 | 12 | 9 | 9 | 2 | N* | N* | 1.015 | 1.040 |
| DU | 0.30 | 18 | 8 | 1 | 1 | 1.00 | 1.22 | 1.02 | 1.26 |

"N" indicates specimen being nonmagnetic (perm. less than 1.01) and "VW" very weakly magnetic (perm. 1.03 or less) as judged with a strong hand magnet.

with the equipment. This alloy, when aged 24 hours at 1400 degrees Fahr. (760 degrees Cent.), showed a magnetic permeability of 2.15 in the deformed section of the tension test specimen. The high strength of this specimen after aging 500 hours at 1200 degrees Fahr. (650 degrees Cent.) was also in line with this discussion, that is, the alloy had become more or less martensitic on aging at 1200 degrees Fahr. (650 degrees Cent.).

The general trend is for the alloys aged 500 hours at 1200 degrees Fahr. (650 degrees Cent.) to show higher strength and lower ductility than the same alloys aged 24 hours at 1400 degrees Fahr. (760 degrees Cent.). This is also true for the 18-8 alloy. In addition to Alloy GQ, three other alloys, FQ, FH, and FV, show

ductility values below 10 after aging at 1200 degrees Fahr. (650 degrees Cent.) for 500 hours. Alloy FQ, on the basis of its composition and the curves in Fig. 7, should be stably austenitic. How-

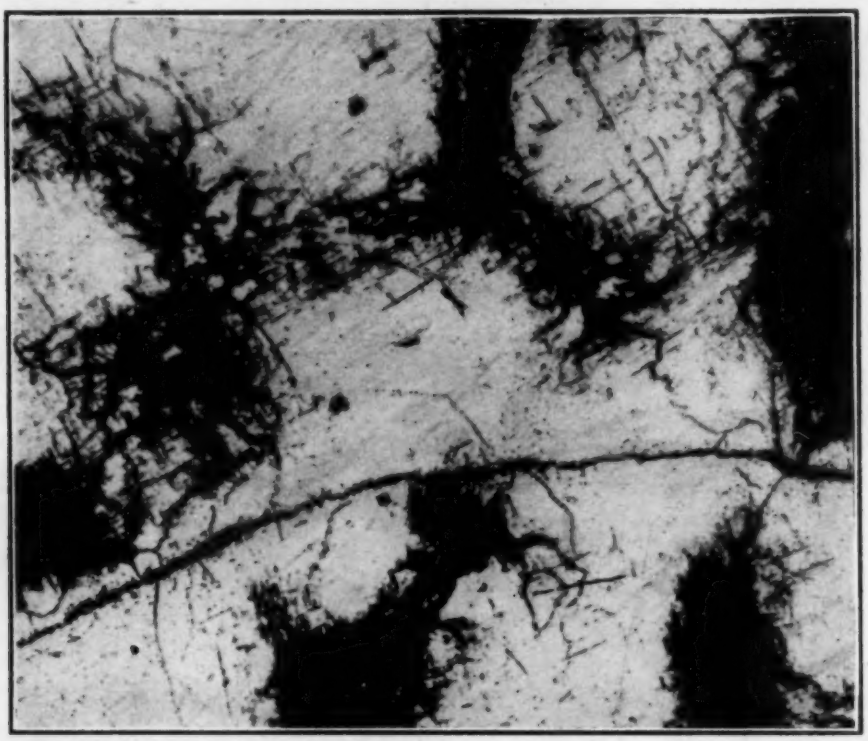

Fig. 8—Photomicrograph of Alloy GK. Aged 500 Hours at 1200 Degrees Fahr. and Tested in Tension at Room Temperature. The Matrix is Austenite with Some Precipitated Carbides. Magnetic Permeability 1.00. × 500.

ever, on aging 500 hours at 1200 degrees Fahr. (650 degrees Cent.), the magnetic permeability in the deformed section of the tension test bar was 1.14 which shows that this alloy is not entirely stable. In connection with Alloy FQ, it is to be noted, however, that the elongation after aging 24 hours at 1400 degrees Fahr. (760 degrees Cent.) was only 10.5 per cent and the reduction of area 11.1 per cent and that these values were not greatly reduced on aging 500 hours at 1200 degrees Fahr. (650 degrees Cent.), the values in this condition being 7.5 and 9.7 per cent, respectively. This alloy contains only 6 per cent nickel. Reference to Fig. 4 will show, as has been pointed out, that the ductility of these alloys increases with the nickel content and that alloys with only 6 per cent nickel have relatively low ductilities even when the manganese content is sufficient to make the alloys stably austenitic. Thus, Alloy FQ, which may be described as substantially stably austenitic,

has low ductility because of its relatively low nickel content and there is comparatively little loss in ductility on long-time aging at 1200 degrees Fahr. (650 degrees Cent.), a temperature which has been found to be most damaging to the ductility of alloys of this type.

Alloy FH has been discussed earlier in this paper and is shown to be too low in manganese to be wholly austenitic. Similarly FV-2 is shown by its composition to be outside the range of the stably

Fig. 9—Photomicrograph of Alloy FE-1. Aged 500 Hours at 1200 Degrees Fahr. and Tested in Tension at Room Temperature. The Matrix is Partly Transformed to Martensite (Ferrite). Magnetic Permeability 1.60. × 500.

austenitic alloys, and this is in agreement with the magnetic permeability tests shown in Table IX.

These data seem to show that the stably austenitic alloys retain their ductility on aging both at 1400 degrees Fahr. (760 degrees Cent.), and at 1200 degrees Fahr. (650 degrees Cent.), but as the alloys depart from the required balance in composition, they show unstable austenite, especially on cold working as in the tension test, and if the manganese is as much as 2 per cent or more less than that indicated by the graph of Fig. 7, the alloys may transform extensively and show low ductility.

The stable austenite character of Alloy GK is evident from the permeability data in Table IX. The data for Alloy FE-1 show that it becomes slightly ferritic on aging 500 hours at 1200 degrees Fahr. (650 degrees Cent.), but the most significant fact is the high permeability shown by the plastically deformed section of Alloy FE-1. This is a characteristic of some of these alloys which are more or less borderline compositions. The microstructures of the alloys also tend to show that Alloys GK and FE-1 differ in the stability of the austenite. The microstructures are given in Figs. 8 and 9. The light matrix of Alloy FE-1 has a roughened acicular appearance, while the matrix of Alloy GK is quite smooth but contains small specks of precipitated carbide throughout.[3] Reference to the magnetic permeability data shows that Alloy FE-1 was only slightly magnetic after the long-time aging treatment, but became rather strongly magnetic in the reduced section (shown in Fig. 9) during the tension test. A transformation under these conditions would be expected to form "white" martensite, and such a structure is frequently difficult to bring out clearly in a photomicrograph. It appears that the magnetic permeability tests and the microstructures are consistent and that certain of the alloys transform more or less, under the influence of plastic deformation, from austenite to martensite.

## Creep Tests

The results of creep tests are given in Table X. Creep curves are shown in Figs. 10 to 12. The data are insufficient for a complete appraisal of the creep characteristics of these alloys, but enough data have been obtained to make comparisons of the load-carrying capacities of these alloys at 1400 degrees Fahr. (760 degrees Cent.) with the "HH" type of alloys at 1800 degrees Fahr. (980 degrees Cent.). A fair indication is also available of the load-carrying capacities of the alloys under study at 1600 degrees Fahr. (870 degrees Cent.). Data for the load-carrying capacities of the "HH" type alloys are available from the publications by Avery, Cook, and Fellows (3) and by Gow and Harder (4).

Two alloys containing approximately 10 per cent chromium

[3]The etching reagent used in the preparation of the photomicrographs shown in Figs. 8, 9, 13, 14, and 15 was a freshly prepared solution containing 5 parts of concentrated hydrochloric acid and 1 part of concentrated nitric acid. The etching time varied and had to be determined by the metallographer for each specimen. While the large dark areas shown in Figs. 8 and 9 and to some extent in Figs. 13, 14, and 15 are not pertinent to the present discussion, they are thought to be finely divided carbides which are overetched because of the necessity of bringing out the structure of the matrix.

(FH and FE-1) have been tested at 1400 degrees Fahr. (760 degrees Cent.). Alloy FH, which is the less stably austenitic alloy, is indicated (Fig. 10) to have a load-carrying capacity for a minimum rate of deformation corresponding to 1 per cent in 10,000 hours of slightly less than 4000 pounds per square inch. Alloy FE-1, which is more nearly a stably austenitic alloy, has a substantially higher load-carrying capacity. For example, its minimum rate of deformation (0.00011 per cent per hour) under a

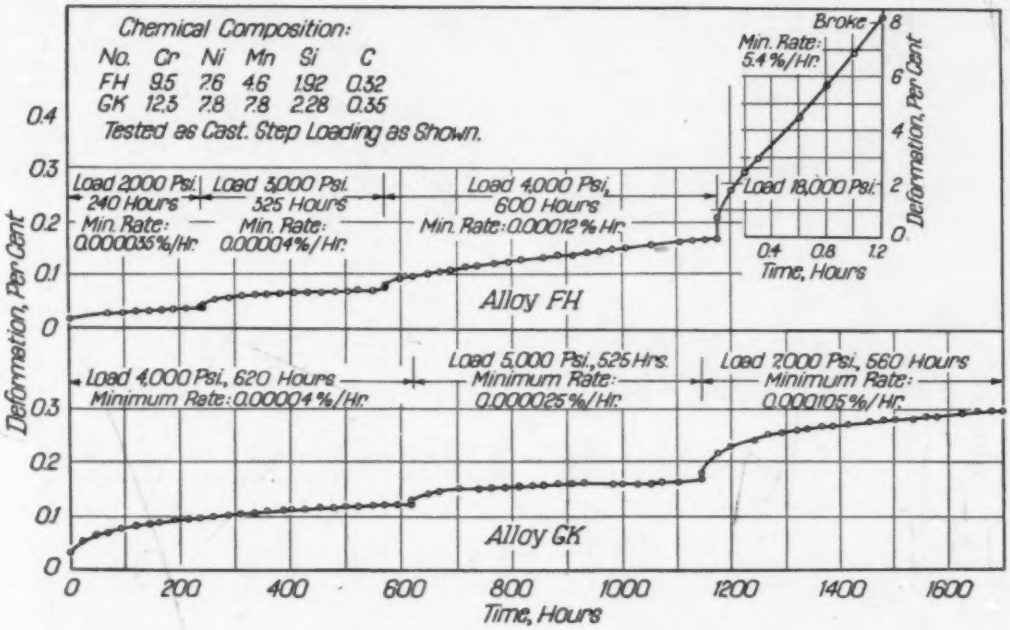


Fig. 10—Creep Tests at 1400 Degrees Fahr.

load of 6000 pounds per square inch is slightly less than for FH (0.00012 per cent per hour) under a load of only 4000 pounds per square inch. Alloy GK is of the 12 per cent chromium type and contains sufficient amounts of nickel and manganese that it is an entirely stable austenite, that is, it is stable after long-time aging and even in the cold deformed section of a tensile test specimen. The creep data for this alloy at 1400 degrees Fahr. (760 degrees Cent.) indicate an L.C.S.[4] value of close to 7000 pounds per square inch. It showed a minimum creep rate of 0.000105 per cent per hour at this load.

For comparison purposes, the data for two alloys of the "HH" type (25 per cent chromium, 12 per cent nickel) from the

[4]A minimum rate of creep corresponding to 1 per cent deformation in 10,000 hours.

**Table X**
**Results of Creep Tests**

| Alloy No. | Composition—Per Cent C | Cr | Ni | Mn | Si | Conditions of Test: Temp. Degrees Fahr. | Load Psi. | Duration Hours | Deformation in Test: Initial Per Cent | Min. Rate Per Cent Per Hour | Final Rate Per Cent Per Hour | Total Per Cent |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| FH | 0.32 | 9.5 | 7.6 | 4.6 | 1.92 | 1400 | 2000 | 242 | 0.017 | 0.000035 | 0.000035 | 0.036 |
| | | | | | | | 3000 | 329 | +0.007 | 0.00004 | 0.00004 | +0.037 |
| | | | | | | | 4000 | 604 | +0.0065 | 0.00012 | 0.00012 | +0.092 |
| | | | | | | Total | | 1175 | | | | 0.165 |
| FH-2 | 0.32 | 10 | 8 | 5 | 2 | 1600 | 2000 | 552 | 0.020 | 0.00017 | 0.00043 | 0.205 |
| FE-1 | 0.32 | 10.0 | 7.0 | 6.1 | 1.96 | 1400 | 4000 | 854 | 0.028 | 0.000035 | 0.000035 | 0.155 |
| | | | | | | | 6000 | 936 | +0.009 | 0.00011 | 0.00014 | +0.160 |
| | | | | | | Total | | 1790 | | | | 0.315 |
| GH-2 | 0.32 | 12 | 9 | 3 | 2 | 1400 | 4000 | 672 | 0.030 | 0.000023 | 0.000023 | 0.110 |
| | | | | | | | 6000 | 428 | +0.016 | 0.00006 | 0.00006 | +0.077 |
| | | | | | | Total | | 1100 | | | | 0.187 |
| GS | 0.32 | 12 | 9 | 5 | 2 | 1400 | 4000 | 600 | 0.032 | 0.000045 | 0.000045 | 0.112 |
| GK | 0.35 | 12.3 | 7.8 | 7.8 | 2.28 | 1400 | 4000 | 623 | 0.031 | 0.00004 | 0.00004 | 0.119 |
| | | | | | | | 5000 | 525 | +0.0085 | 0.000025 | 0.000025 | +0.043 |
| | | | | | | | 7000 | 555 | +0.022 | 0.000105 | 0.000105 | +0.139 |
| | | | | | | Total | | 1703 | | | | 0.301 |
| | | | | | | 1600 | 2500 | 319 | 0.030 | 0.000065 | 0.000065 | 0.066 |
| | | | | | | | 3000 | 817 | +0.004 | 0.000115 | 0.000115 | +0.130 |
| | | | | | | Total | | 1136 | | | | 0.196 |
| DU-2 | 0.32 | 18 | 8 | 1 | 1 | 1400 | 7000 | 1012 | 0.057 | 0.000035 | 0.000035 | 0.220 |
| | | | | | | 1600 | 2000 | 384 | 0.017 | 0.00000 | 0.00000 | |
| | | | | | | | 3000 | 238 | +0.011 | 0.00001 | 0.00001 | |
| | | | | | | | 5000 | 425 | +0.016 | 0.00012 | *Broke* | |
| | | | | | | Total | | 1047 | | | | |
| AS-2[1] | 0.33 | 24.57 | 12.48 | 0.97 | 0.84 | 1800 | 2500 | 1540 | 0.025 | 0.00005 | 0.00020 | 0.170 |
| | | | | | | 1600 | 5000 | 1031 | 0.039 | 0.000095 | 0.0001 | 0.241 |
| AX-1[2] | 0.31 | 27.17 | 11.84 | 0.95 | 0.98 | 1800 | 2000 | 742 | 0.038 | 0.00022 | 0.00031 | 0.193 |
| | | | | | | 1600 | 4000 | 730 | 0.053 | ? | 0.00125 | 1.357 |

[1]Wholly austenitic "HH" type alloy with 0.087 per cent N. Data from paper by Gow and Harder.
[2]Partially ferritic "HH" type alloy.

publication by Gow and Harder (4) are included in Table X. At 1800 degrees Fahr. (980 degrees Cent.), Alloy AS-2, which is wholly austenitic, showed a minimum creep rate of 0.00005 per cent per hour under a load of 2500 pounds per square inch. Avery, Cook, and Fellows (3) have reported L.C.S. values for alloys of the "HH" type and in one tabulation gave values of 600 to 2650 pounds per square inch and in another 600 to 3000 pounds per square inch at 1800 degrees Fahr. (980 degrees Cent.). Even the FH alloy mentioned above shows a somewhat lower minimum rate at 1400 degrees Fahr. (760 degrees Cent.) under a load of 3000 pounds per square inch than AS-2 under a load of 2500 pounds per square inch at 1800 degrees Fahr. (980 degrees Cent.). Alloy FE shows a substantially lower rate under a load of 4000 pounds per square inch and GK a substantially lower rate under a load of 5000 pounds per square inch than did Alloy AS-2 at 1800 degrees Fahr. (980 degrees Cent.) under a load of 2500 pounds per square inch. Thus the load-carrying capacities at 1400 degrees Fahr. (760 degrees Cent.) for the alloys being studied are definitely superior to the load-carrying capacities of the "HH" type at 1800 degrees Fahr. (980 degrees Cent.).

For further comparison purposes a partially austenitic alloy of the "HH" type (AX-1) has also been included in Table X from the publication by Gow and Harder (4). Under a load of 2000 pounds per square inch at 1800 degrees Fahr. (980 degrees Cent.), it showed a minimum rate of 0.00022 per cent per hour, or the equivalent of over 2 per cent in 10,000 hours. The data by Avery, Cook, and Fellows (3) show still lower L.C.S. values as possible for alloys of the "HH" type. Obviously, the comparison of the new alloys with the partially ferritic alloys of the "HH" type would be even more favorable to the new alloys than when the comparison is made with wholly austenitic alloys of the "HH" type.

One alloy, DU, of the 18-8 type has been tested at 1400 degrees Fahr. (760 degrees Cent.). It is indicated to have higher load-carrying capacities at this temperature than any of the new alloys. See Table X and Fig. 11.

The data for the load-carrying capacities of the alloys at 1600 degrees Fahr. (870 degrees Cent.) are somewhat more limited because it was an objective of the original program to develop alloys for use only up to 1400 degrees Fahr. (760 degrees Cent.).

However, some data are available for the load-carrying capacities at 1600 degrees Fahr. (870 degrees Cent.). Alloy FH-2 was tested at 1600 degrees Fahr. (870 degrees Cent.) under a load of 2000 pounds per square inch and showed a minimum rate of 0.00017 per cent per hour with the test run only to 552 hours. (See Fig. 12.) This specimen had entered the third stage of creep at the end of the test. In comparison with the tests on this same alloy at 1400 and at 1600 degrees Fahr. (760 and at 870 degrees Cent.) it will be observed that the load-carrying capacity at 1600

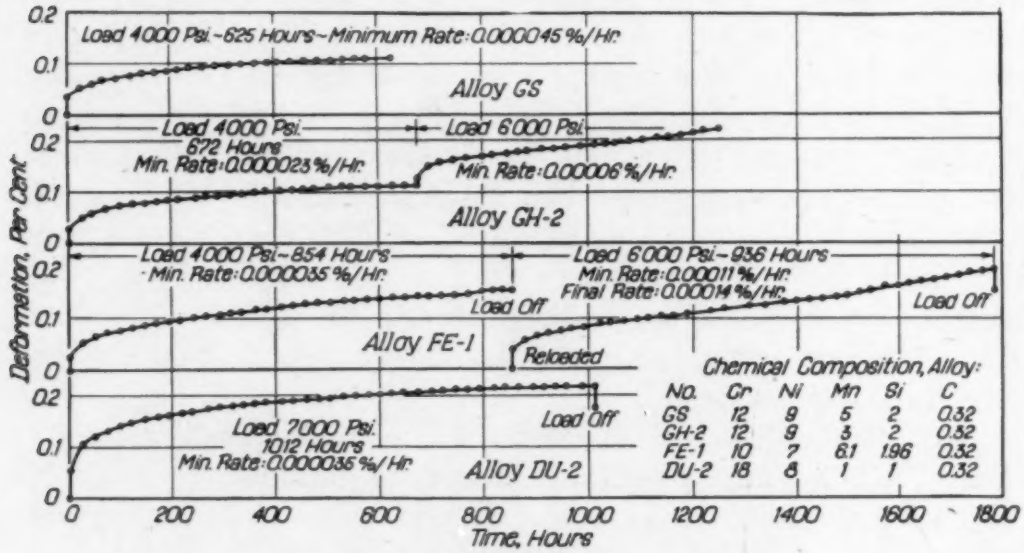


**Fig. 11—Creep Tests at 1400 Degrees Fahr.**

degrees Fahr. (870 degrees Cent.) is less than one-half of what it is at 1400 degrees Fahr. (760 degrees Cent.). Alloy GK has also been tested at 1600 degrees Fahr. (870 degrees Cent.) and is shown to have an L.C.S. value between 2500 and 3000 pounds per square inch. (See Fig. 12.) This alloy is also indicated to have not more than one-half the load-carrying capacity at 1600 degrees Fahr. (870 degrees Cent.) that it does at 1400 degrees Fahr. (760 degrees Cent.). The load-carrying capacity at 1600 degrees Fahr. (870 degrees Cent.), however, is not far from that of the "HH" type of alloy, AS-2, at 1800 degrees Fahr. (980 degrees Cent.) and is definitely higher than the partially ferritic alloy AX-1 of the "HH" type at 1800 degrees Fahr. (980 degrees Cent.).

The 18-8 type of alloy represented by DU-2 is indicated to have a substantially higher load-carrying capacity at 1600 degrees

Fahr. (870 degrees Cent.) than the best of the new alloys tested, Alloy GK. However, it is to be noted that when Alloy DU-2 was tested at a load of 5000 pounds per square inch at 1600 degrees Fahr. (870 degrees Cent.), it broke after 425 hours with a brittle fracture.

From the data now available, it may be stated that the new alloys when stably austenitic have markedly greater load-carrying capacities at 1400 degrees Fahr. (760 degrees Cent.) than do wholly austenitic alloys of the "HH" type at 1800 degrees Fahr.

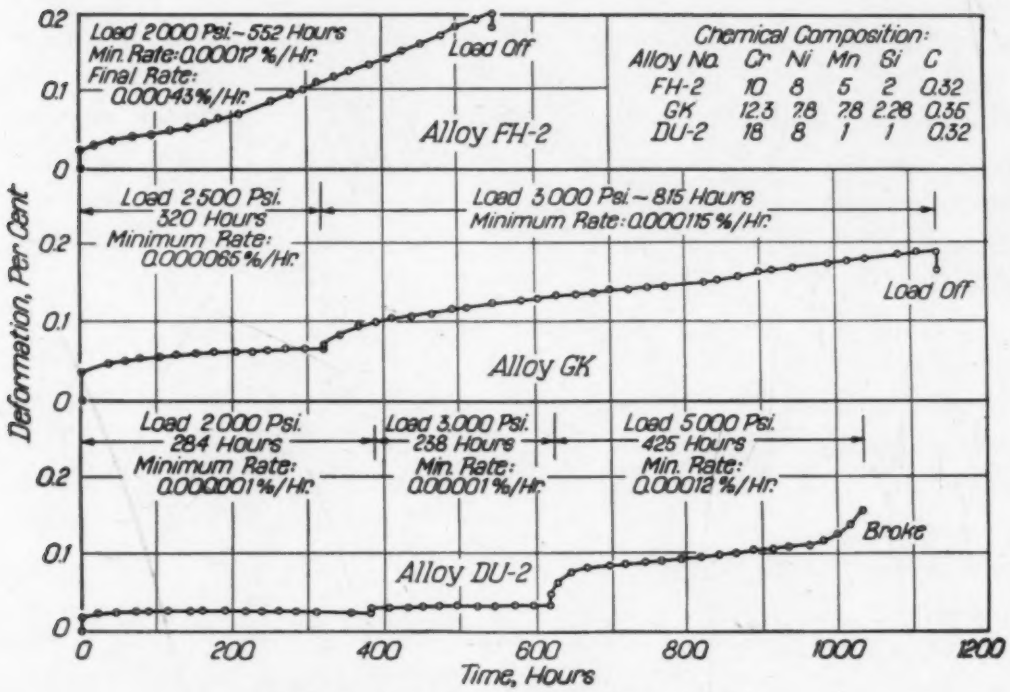


**Fig. 12—Creep Tests at 1600 Degrees Fahr.**

(980 degrees Cent.). Like alloys of the "HH" type, the new alloys, as they depart from the wholly austenitic structure, have lower load-carrying capacities, but it is indicated that an alloy which is not wholly austenitic, such as FH, has a higher load-carrying capacity at 1400 degrees Fahr. (760 degrees Cent.) than do wholly austenitic alloys of the "HH" type at 1800 degrees Fahr. (980 degrees Cent.).

In some cases the new alloys have a load-carrying capacity at 1600 degrees Fahr. (870 degrees Cent.) equal to wholly austenitic alloys of the "HH" type at 1800 degrees Fahr. (980 degrees Cent.). It is thus indicated that the new alloys satisfy one of the

original requirements, that is, a load-carrying capacity at 1400 degrees Fahr. (760 degrees Cent.) at least equivalent to an alloy of the "HH" type at 1800 degrees Fahr. (980 degrees Cent.). In order to further test these alloys, however, tension tests have been made on some of them after being in creep tests. The results are discussed in the following section.

*Residual Properties of Creep Test Specimens* — The results of tests on specimens after they were removed from the creep tests are shown in Table XI. This table gives the compositions of the alloys, the creep test conditions, the residual properties at room temperature after the creep tests, and then for comparison purposes, the room temperature properties of aged alloys. Data also are given for the magnetic permeability of the deformed portion of the creep test specimen after it had been fractured in tension at room temperature and for the specimen aged 24 hours at 1400 degrees Fahr. (760 degrees Cent.) and tested in tension at room temperature.

Alloy FH at the end of the creep test was used for a stress-time-rupture test. (See Fig. 10.) As a result, its room temperature properties after creep are not available. The deformed portion of the creep test specimen showed a magnetic permeability of 1.46. This permeability is substantially higher than a similar section from a specimen, of essentially the same composition (FH-2), which had been aged 24 hours at 1400 degrees Fahr. (760 degrees Cent.) and tested in tension at room temperature.

Alloy FE-1, after a creep test at 1400 degrees Fahr. (760 degrees Cent.) extending over 1790 hours, showed higher ultimate strength than as aged. The yield strength, however, was lower, but the elongation was 21.5 per cent as compared with 14 per cent on the aged alloy. This alloy became highly magnetic in the deformed portion of the creep test bar giving a value of 4+.

Alloy GK after being tested for 1700 hours at 1400 degrees Fahr. (760 degrees Cent.) showed some loss in ultimate strength and the same yield strength, but both the elongation and reduction in area values were decreased somewhat. Even the deformed section of this specimen was nonmagnetic with a permeability of 1.00.

Alloy DU-2 in a creep test at 1400 degrees Fahr. (760 degrees Cent.), under a load of 7000 pounds per square inch for over 1000 hours, showed substantially no change in ultimate and yield strengths and only moderate reductions in elongation and reduction

of area values. It showed a magnetic permeability of 1.16 in the deformed section.

Only two of the emergency alloys have been tested in creep at 1600 degrees Fahr. (870 degrees Cent.). Alloy GK showed a reduction in all of the strength properties after it had been tested at 1600 degrees Fahr. (870 degrees Cent.) for 1136 hours. The strength after testing at 1600 degrees Fahr. (870 degrees Cent.) was substantially lower than after testing at 1400 degrees Fahr. (760 degrees Cent.). These periods of exposure to creep test resulted

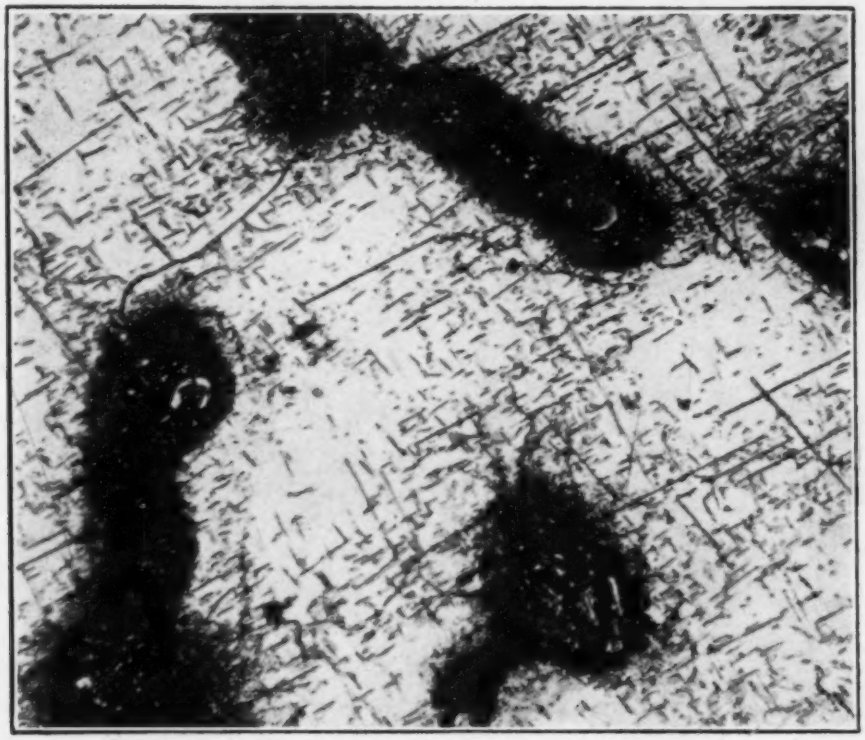

Fig. 13—Photomicrograph of Alloy GK. After Creep Test—1703 Hours at 1400 Degrees Fahr. × 500.

in some loss of section because of scaling. However, it is indicated there was actual loss in strength. Alloy FH-2 showed a marked loss in room temperature strength after being subjected to a creep test at 1600 degrees Fahr. (870 degrees Cent.) under a load of 2000 pounds per square inch. Examination of the creep curve (Fig. 12) of this alloy will show that this specimen had reached Stage III even at the end of 150 hours. The composition of Alloy FH-2 is rather close to that of FE-1, and the data show that this alloy did not lose in its room temperature strength because of

**Table XI**

**The Residual Properties of Creep Test Specimens and Initial Properties for Comparison**

| Alloy No. | Creep Test Conditions: Temp. Degrees Fahr. | Load Psi. | Time Hours | Deformation Total Per Cent | Residual Mechanical Properties of Creep Test Bars | Initial Properties of Materials | Magnetic Permeability of Fractured Test Specimens: Creep Test Deformed Portion | 24 Hours 1400 Degrees Fahr. Aged Alloy: Not Deformed | Deformed |
|---|---|---|---|---|---|---|---|---|---|
| FH | 1400 | 2000 | 242 | | Stress-Time-Rupture Data at 1400° F. | 1400° F. Tension Test Results | | | |
| C — 0.32 | | 3000 | 329 | | | | | | |
| Cr — 9.5 | | 4000 | 604 | | Stress, psi.—18,000 | Tensile Strength, psi.—27,200 | | | |
| Ni — 7.6 | | | 1175 | 0.165 | Time to Fracture—1.4 Hrs. | | | | |
| Mn — 4.6 | | | | | | Yield Strength (0.2 Per Cent Def.)—19,900 | 1.46 | 1.01 | 1.14 |
| Si — 1.92 | | | | | Elongation—8+ Per Cent | Elongation, Per Cent—22 | | | |
| | | | | | | Reduction of Area, Per Cent—28.2 | | | |
| FH-2 | 1600 | 2000 | 552 | 0.205 | Room Temp. Tens. Test Data | "Aged" Alloy Tested at R.T. | | | |
| C — 0.32 | | | | | | | | | |
| Cr — 10 | | | | | Tensile Strength—66,000 | Tensile Strength, psi.—91,200 | | | |
| Ni — 8 | | | | | Yield Strength (0.2 Per Cent. Def.)—34,500 | Yield Strength (0.2 Per Cent Def.) psi.—43,100 | 2.19 | .... | .... |
| Mn — 5 | | | | | Elongation, Per Cent—12.0 | Elongation, Per Cent—19.0 | | | |
| Si — 2 | | | | | Reduction of Area—18.8 | Reduction of Area—23.4 | | | |
| FE-1 | 1400 | 4000 | 854 | | | "Aged" Alloy Tested at R.T. | | | |
| C — 0.32 | | 6000 | 936 | | Tensile Strength, psi.—100,500 | Tensile Strength, psi.—93,300 | | | |
| Cr — 10.0 | | | 1790 | 0.315 | Yield Strength (0.2 Per Cent Def.) psi.—35,500 | Yield Strength (0.2 Per Cent Def.) psi.—47,400 | 4.+ | 1.01 | 1.03 |
| Ni — 7.0 | | | | | Elongation, Per Cent—21.5 | Elongation, Per Cent—14.0 | | | |
| Mn — 6.1 | | | | | Reduction of Area, Per Cent—9.2 | Reduction of Area—16.0 | | | |
| Si — 1.96 | | | | | | | | | |

Table XI—(Continued)

| Alloy No. | Creep Test Conditions: Temp. Degrees Fahr. | Load Psi. | Time Hours | Deformation Total Per Cent | Residual Mechanical Properties of Creep Test Bars | Initial Properties of Materials | Magnetic Permeability of Fractured Test Specimens: Creep Test Deformed Portion | 24 Hours 1400 Degrees Fahr. Aged Alloy: Not Deformed | Deformed |
|---|---|---|---|---|---|---|---|---|---|
| GK<br>C — 0.35<br>Cr — 12.3<br>Ni — 7.8<br>Mn — 7.8<br>Si — 2.28 | 1400 | 4000<br>5000<br>7000 | 623<br>525<br>555<br>1703 | 0.301 | Tensile Strength, psi.—80,800<br>Yield Strength (0.2 Per Cent Def.) psi.—44,000<br>Elongation, Per Cent—6.5<br>Reduction of Area, Per Cent—12.3 | "Aged" Alloy Tested at R.T.<br>Tensile Strength, psi.—91,200<br>Yield Strength (0.2 Per Cent Det.) psi.—43,100<br>Elongation, Per Cent—19.0<br>Reduction of Area, Per Cent—23.4 | 1.00 | 1.00 | 1.00 |
| GK<br>Composition as above | 1600 | 2500<br>3000 | 319<br>817<br>1136 | 0.196 | Tensile Strength, psi.—73,600<br>Yield Strength (0.2 Per Cent Def.) psi.—39,000<br>Elongation, Per Cent—7.0<br>Reduction of Area, Per Cent—11.1 | See above data. | 1.00 | 1.00 | 1.00 |
| DU-2<br>C — 0.32<br>Cr — 18<br>Ni — 8<br>Mn — 1<br>Si — 1 | 1400 | 7000 | 1012 | 0.190 | Tensile Strength, psi.—98,600<br>Yield Strength (0.2 Per Cent Def.) psi.—46,750<br>Elongation, Per Cent—20<br>Reduction of Area, Per Cent—15.2 | "Aged" Alloy Tested at R.T.<br>Tensile Strength, psi.—97,100<br>Yield Strength (0.2 Per Cent Def.) psi.—45,000<br>Elongation, Per Cent—25.5<br>Reduction of Area, Per Cent—20.6 | 1.16 | 1.00 | 1.22 |

having been stressed in creep at 1400 degrees Fahr. (760 degrees Cent.) for 1790 hours. Thus stressing in creep at 1600 degrees Fahr. (870 degrees Cent.) seems to reduce the room temperature strength of these alloys much more than does stressing at 1400 degrees Fahr. (760 degrees Cent.).

Alloy DU-2 was tested in creep at 1600 degrees Fahr. (870 degrees Cent.) under a load of 5000 pounds per square inch, but

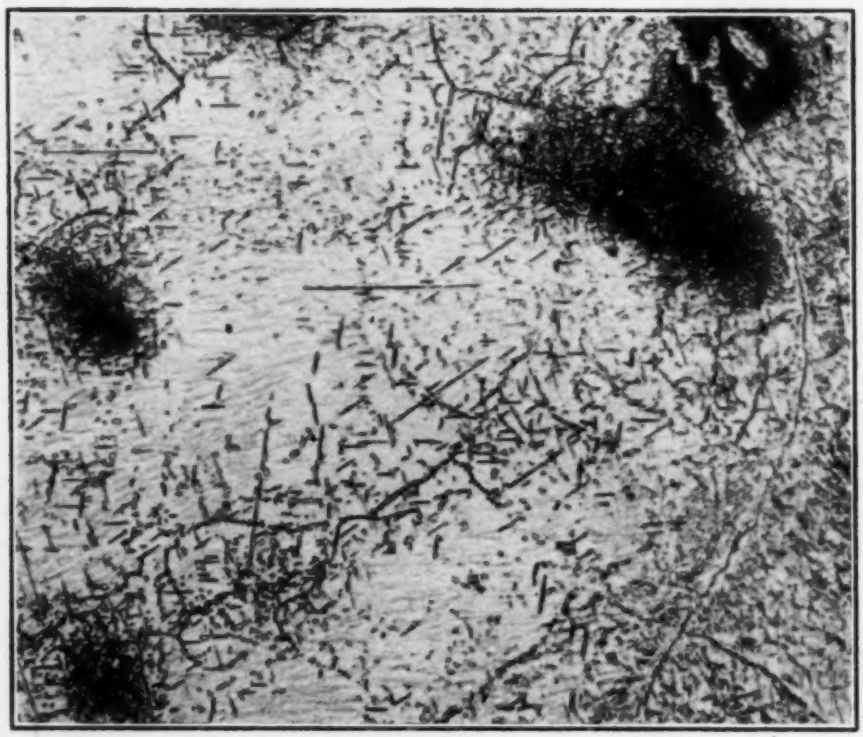

Fig. 14—Photomicrograph of Alloy FH. After Creep Test—1175 Hours at 1400 Degrees Fahr. × 500.

since it failed in the creep test with a brittle fracture, no data are available for its residual strength properties. It is to be noted that this 18-8 alloy (DU-2) is not stably austenitic under all conditions because it showed magnetic permeabilities of 1.16 and 1.22 in the deformed sections of tension test specimens after creep and after aging 24 hours at 1400 degrees Fahr. (760 degrees Cent.), respectively. Further work is needed on the 18-8 type of alloy to determine to what extent the brittle type of failure noted at 1600 degrees Fahr. (870 degrees Cent.) may be encountered and to determine if this type of failure may be encountered at 1400 degrees Fahr. (760 degrees Cent.) when the load is sufficient to produce greater rates of creep than have been obtained in the

present tests. There is also interest in the 18-8 type of alloy with lower carbon contents, such as about 0.20 to 0.25 per cent, which are more common in industry.

*Microstructures of Creep Test Specimens* — The microstructures of the creep test specimens have been studied using the deformed section of specimens tested in tension at room temperature after the creep test. Figs. 13, 14, and 15 represent the structures

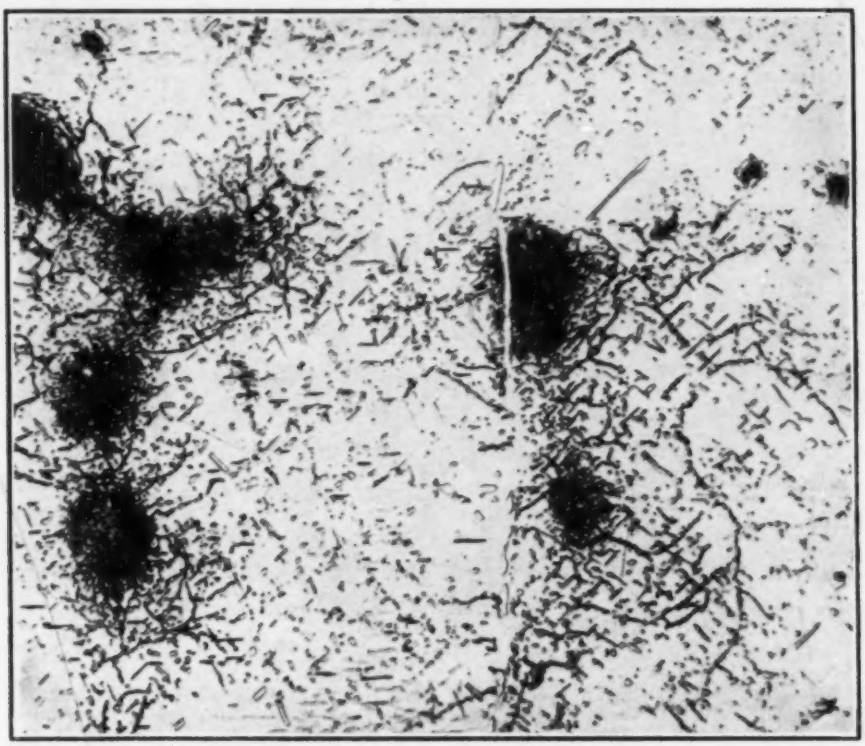

Fig. 15—Photomicrograph of Alloy GK. After Creep Test—1136 Hours at 1600 Degrees Fahr. × 500.

of Alloys GK and FH tested in creep at 1400 degrees Fahr. (760 degrees Cent.) and Alloy GK tested at 1600 degrees Fahr. (870 degrees Cent.), respectively. Alloy GK after 1703 hours at 1400 degrees Fahr. (760 degrees Cent.) and under the loads shown in Table X shows carbides and some markings from cold deformation as shown in Fig. 13. This alloy was wholly austenitic after these tests. On the other hand, Alloy FH became rather highly magnetic (permeability 1.46) after these tests. Its structure (Fig. 14) shows acicular roughening of the matrix, which is interpreted to indicate some transformation of the austenite to martensite.

Fig. 15 shows the structure of Alloy GK after being tested in creep at 1600 degrees Fahr. (870 degrees Cent.) for 1136 hours

and then broken in tension at room temperature. Comparison of the structures in Figs. 15 and 13 shows definite evidence of agglomeration of the carbides in this alloy at 1600 degrees Fahr. (870 degrees Cent.), and this is consistent with the loss in room temperature strength resulting from exposure at 1600 degrees Fahr. (870 degrees Cent.) as shown in Table X. This specimen was entirely non-magnetic.

## Oxidation Tests

Oxidation tests were made at 1400 and 1600 degrees Fahr. (760 and 870 degrees Cent.) by heating in an electric furnace for 120 hours and then determining the weight loss by removing the scale electrolytically in a fused salt bath. The results are given in Tables XII and XIII. For comparison purposes, six alloys of the "HH" type, from the paper by Gow and Harder (4), were tested under similar conditions but at a temperature of 2000 degrees Fahr. (1095 degrees Cent.). The purpose was to compare the weight loss of alloys of this type run at a high temperature with the weight loss of the alloys being studied at 1600 degrees Fahr. (870 degrees Cent.), which was considered a comparable high temperature for the new alloys. While the majority of these tests were made under conditions of continuous heating and did not determine what would be the effect of intermittent heating and cooling, some few tests were made in order to get information along this line. Six alloys with a chromium content of 10 per cent and six with a chromium content of 12 per cent were subjected to cyclic heating with 18 minutes at the maximum temperature of 1400 degrees Fahr. (760 degrees Cent.) and 2 minutes out of the furnace, which cooled the specimen to a black heat. The results are given in Table XIV.

The results of oxidation tests on a group of specimens which do not fall within the range of composition finally selected are given in Table XII. There is special interest in Alloys C-32, C-28, EB, and EA. Alloys C-32 and C-28 were supplied by member companies and are representative of the 5 to 6 per cent chromium with about 0.5 per cent of molybdenum and alloys which might be specified for temperatures up to 1400 degrees Fahr. (760 degrees Cent.) by Supplementary Order M-21-g. It will be noted that these alloys, with the exception of EA, showed high weight losses at 1600 degrees Fahr. (870 degrees Cent.), but fairly good resistance

to oxidation at 1400 degrees Fahr. (760 degrees Cent.). While these alloys might be acceptable from the standpoint of resistance to oxidation at 1400 degrees Fahr. (760 degrees Cent.), the results of bend tests discussed earlier in this paper showed that Alloys EA and EB were too brittle for satisfactory handling in the foundry. Such alloys are being produced, however.

**Table XII**
**Oxidation Tests at 1400 and 1600 Degrees Fahr.[1]**

| Alloy No. | Composition—Per Cent | | | | | | Weight Loss[2] Grams Per Sq. In. Per 24 Hours | |
|---|---|---|---|---|---|---|---|---|
| | Cr | Ni | Mn | Si | C | Others | at 1400 Deg. Fahr. | at 1600 Deg. Fahr. |
| C-32 | 5.77 | . | 0.49 | 0.81 | 0.16 | 0.5 Mo, 0.49 Cb | 0.006 | 0.185 |
| C-28 | 5.11 | . | 0.61 | 1.44 | 0.20 | 0.53 Mo | 0.006 | 0.125 |
| EB | 6 | . | 1 | 1.5 | 0.20 | 1.5 Cu | 0.0020 | 0.342 |
| EA | 6 | . | 1 | 2 | 0.30 | 0.5 Mo | 0.0039 | 0.0031 |
| EF | 10 | . | 1 | 1 | 0.30 | 2 Al | 0.0007 | 0.0027 |
| C-30 | 12.4 | . | 0.60 | 0.42 | 0.15 | .... | 0.005 | 0.218 |
| C-31 | 12.1 | . | 0.51 | 0.38 | 0.26 | .... | 0.004 | 0.260 |
| C-41 | 12.4 | . | 0.47 | 0.48 | 0.13 | 0.51 Mo, 0.55 Cb | 0.005 | 0.076 |
| EC | 12 | . | 0.5 | 2 | 0.30 | 0.5 Mo | 0.0016 | 0.0054 |
| ED | 12 | . | 0.5 | 2 | 0.30 | 0.5 Mo, 1 Cb | 0.0015 | 0.0039 |
| DQ | 10 | 2 | 2 | 1 | 0.30 | 2 Cu | 0.006 | ..... |
| DR | 10 | 2 | 2 | 2 | 0.49 | 2 Cu | 0.004 | ..... |
| DS | .. | . | 10 | 2 | 0.3 | .... | 0.128 | 0.276 |
| DT | .. | . | 10 | 4 | 0.3 | .... | ..... | 0.015 |
| DA | 6 | 4 | 5 | 1 | 0.31 | .... | 0.090 | 0.374 |
| DB | 6 | 4 | 10 | 2 | 0.47 | .... | 0.096 | 0.295 |
| DC | 6 | 4 | 15 | 1 | 0.29 | .... | 0.121 | 0.295 |
| DD | 6 | 8 | 5 | 1 | 0.30 | .... | 0.078 | 0.314 |
| EG | 6 | 8 | 5 | 2 | 0.30 | .... | 0.074 | 0.223 |
| EH | 6 | 8 | 10 | 2 | 0.30 | .... | 0.065 | 0.256 |
| DE | 6 | 8 | 10 | 2 | 0.51 | .... | 0.008 | 0.249 |
| DF | 6 | 8 | 15 | 1 | 0.31 | .... | 0.117 | 0.577 |

[1]Continuous exposure for 120 hours.
[2]Scale removed electrolytically in fused salt bath. Specimens were ¼ x ¾ x 1½-inch flats.

Alloys C-30, C-31, and C-41 represent materials, produced by member companies, with 12 per cent chromium. Again the oxidation resistance at 1600 degrees Fahr. (870 degrees Cent.) is generally unsatisfactory, and as previously pointed out, similar alloys failed to meet requirements on the basis of bend tests. The last 8 alloys in this table are 6 per cent chromium with additions of nickel and manganese. It is obvious that their resistance to oxidation at 1600 degrees Fahr. (870 degrees Cent.) is bad and is rather poor even at 1400 degrees Fahr. (760 degrees Cent.). Thus the general picture for alloys of only 6 per cent chromium is that their resistance to oxidation is relatively poor when the silicon content is about 1 per cent, is somewhat better with 2 per cent;

but furthermore most of these alloys are rated as too brittle for satisfactory handling in the foundry. Even the 12 per cent alloys of normal silicon contents have poor resistance to oxidation at

**Table XIII**
**Oxidation Tests at 1400 and 1600 Degrees Fahr.[1]**

| Alloy No. | Composition—Per Cent | | | | | Weight Loss[2] Grams Per Sq. In. Per 24 Hours | |
|---|---|---|---|---|---|---|---|
| | Cr | Ni | Mn | Si | C | At 1400 Degrees Fahr. | At 1600 Degrees Fahr. |
| DG | 10 | 4 | 5 | 1 | 0.30 | 0.067 | 0.189 |
| DH | 10 | 4 | 10 | 2 | 0.50 | 0.010 | 0.003 |
| DI | 10 | 4 | 15 | 1 | 0.31 | 0.032 | 0.201 |
| EI | 10 | 6 | 10 | 2 | 0.50 | 0.0025 | 0.076 |
| GA | 10 | 7 | 6 | 2.5 | 0.40 | ..... | 0.029 |
| GC | 10 | 8 | 3 | 2 | 0.33 | ..... | 0.045 |
| EJ | 10 | 8 | 5 | 2 | 0.30 | 0.0021 | 0.015 |
| EK | 10 | 8 | 5 | 2 | 0.50 | 0.0015 | 0.047 |
| EM[3] | 10 | 8 | 5 | 1 | 0.30 | 0.0063 | 0.130 |
| EN[3] | 10 | 8 | 5 | 2 | 0.30 | 0.0013 | 0.003 |
| DJ | 10 | 8 | 5 | 1 | 0.31 | 0.032 | 0.136 |
| DK | 10 | 8 | 10 | 2 | 0.59 | 0.005 | 0.004 |
| EL | 10 | 8 | 10 | 3 | 0.50 | 0.001 | 0.003 |
| DL | 10 | 8 | 15 | 1 | 0.32 | 0.015 | 0.157 |
| GD | 10 | 9 | 3 | 2 | 0.33 | ..... | 0.065 |
| GE | 10 | 9 | 5 | 2 | 0.33 | ..... | 0.017 |
| EQ | 12 | 4 | 10 | 2 | 0.30 | 0.001 | 0.003 |
| DM | 12 | 6 | 1 | 1 | 0.53 | 0.004 | 0.049 |
| DN | 12 | 6 | 4 | 1 | 0.50 | 0.121 | 0.066 |
| EP | 12 | 6 | 4 | 2 | 0.50 | 0.0015 | 0.003 |
| DO | 12 | 6 | 8 | 1 | 0.49 | 0.004 | 0.023 |
| DP | 12 | 6 | 8 | 2 | 0.49 | 0.002 | 0.008 |
| EQ | 12 | 6 | 8 | 3 | 0.50 | 0.001 | 0.002 |
| ER | 12 | 6 | 10 | 2 | 0.50 | 0.0015 | 0.003 |
| ES | 12 | 6 | 10 | 3 | 0.50 | 0.0015 | 0.002 |
| ET | 12 | 6 | 10 | 4 | 0.50 | 0.003 | 0.002 |
| GF | 12 | 8 | 3 | 2 | 0.33 | ..... | 0.007 |
| GK | 12 | 8 | 8 | 2 | 0.33 | ..... | 0.007 |
| GH | 12 | 9 | 3 | 2 | 0.33 | ..... | 0.008 |
| GG | 12 | 9 | 4 | 2 | 0.33 | ..... | 0.007 |
| GI | 12 | 10 | 3 | 2 | 0.33 | ..... | 0.011 |
| GJ | 12 | 10 | 5 | 2 | 0.33 | ..... | 0.006 |
| GB | 13 | 9 | 9 | 1.5 | 0.30 | ..... | 0.006 |
| DU[4] | 18 | 8 | 1 | 1 | 0.30 | 0.003 | 0.002 |
| DW[4] | 18 | . | 10 | 1 | 0.35 | 0.001 | 0.005 |
| DV[4] | 18 | 4 | 6 | 1 | 0.32 | 0.003 | 0.012 |
| EU | 18 | 4 | 6 | 2 | 0.40 | 0.003 | 0.002 |
| EV | 18 | 6 | 4 | 2 | 0.40 | 0.0015 | 0.0015 |
| EW | 18 | 6 | 6 | 2 | 0.30 | 0.002 | 0.0015 |
| DX[4] | 24 | 12 | 1 | 1 | 0.38 | 0.001 | 0.002 |

[1]Continuous exposure for 120 hours.
[2]Scale removed eelctrolytically in a fused-salt bath. Specimens were ¼ x ¼ x1½-inch flats.
[3]Contained 2 per cent copper.
[4]Intended nitrogen—0.07 per cent.

1600 degrees Fahr. (870 degrees Cent.). If it were permissible to take these 6 per cent chromium alloys and add nickel and manganese, the oxidation resistance at 1600 degrees Fahr. (870 degrees Cent.) would be relatively poor.

The results of oxidation tests of the alloys of special interest are given in Table XIII. As in previous tests, they are grouped according to chromium content and then, under a given chromium content, at different nickel levels with variations in manganese and/or silicon. Before discussing the corrosion resistance of these alloys, reference should be made to Table XIV which gives the results of corrosion tests at 2000 degrees Fahr. (1095 degrees Cent.) on six alloys of the "HH" type. The average weight loss expressed in grams per square inch per day is 0.0151. This value then may be used for discussion of the alloys listed in Table XIII when the tests were made at 1600 degrees Fahr. (870 degrees Cent.). It is clearly shown that silicon is supplementary to chromium in developing resistance to oxidation. The resistance is increased particularly as the silicon content is increased from 1 to 2 per cent. There

**Table XIV**
**Oxidation Test Results for HH Type Alloys**
(Exposure Temperature 2000 Degrees Fahr.; Time—120 Hours)

| Alloy No. | Composition—Per Cent | | | | | Metal Loss by Scaling[1] Grams Per Sq. In. Per Day |
|---|---|---|---|---|---|---|
| | C | Ni | Cr | Mn | Si | |
| AA | 0.40 | 11.20 | 24.75 | 0.90 | 1.03 | 0.0107 |
| AS-1 | 0.33 | 12.36 | 24.18 | 0.96 | 0.83 | 0.0124 |
| AX-3 | 0.32 | 10.60 | 23.98 | 0.89 | 0.96 | 0.0176 |
| AX-4 | 0.31 | 10.61 | 26.70 | 0.92 | 1.00 | 0.0133 |
| AW-1 | 0.31 | 11.94 | 24.40 | 0.95 | 0.34 | 0.0238 |
| AW-3 | 0.31 | 12.68 | 24.49 | 0.90 | 1.80 | 0.0127 |
| | | | | | | Average 0.0151 |
| | | | | | | Range 0.0107–0.0238 |

[1]Specimens were ⅜-inch-diameter by 2-inch long cylinders. Scale removed electrolytically in fused salt bath.

is a general trend for further improvement in resistance to oxidation on increasing the silicon to 3 per cent and in some cases to 4 per cent. Previous work has shown, however, that increasing the silicon from 2 to 3 per cent causes loss in ductility, but there is comparatively little loss in ductility on increasing the silicon from 1 to 2 per cent. The effect of increasing the silicon, with other elements of composition held constant, is illustrated by Alloys DN and EP where there is a marked effect on increasing the silicon from 1 to 2 per cent. This effect is also illustrated by comparing Alloys DO, DP, and DQ where the silicon content is increased from 1 to 3 per cent. This effect is particularly noticeable in the tests at 1600 degrees Fahr. (870 degrees Cent.). The general picture of the oxidation resistance of these alloys from the data in Table XIII is as follows: Other elements in composition being the same, alloys of 12 to 13 per cent chromium have better resistance

**Table XV**

**Oxidation Test Results for Alloys Tested Under Conditions of Cyclic Heating and Cooling**

Cycle:
Specimens in furnace at 1400 degrees Fahr.—18 minutes.
Out of furnace in air at room temperature—2 minutes.
Specimens exposed in two groups:
Group 1—FA, FG, FH, FU, FX, FY—
165 hours in test—495 cycles of heating and cooling.
Group 2—FE, FK, FW, FQ, FR, FT—
100 hours in test—300 cycles.

| Alloy No.[1] | Cr Per Cent | Weight Loss[2] | Alloy No.[1] | Cr Per Cent | Weight Loss[2] |
|---|---|---|---|---|---|
| FY | 10 | 0.0053 | FN | 12 | 0.0013 |
| FA | 10 | 0.0017 | FQ | 12 | 0.0013 |
| FE | 10 | 0.0022 | FR | 12 | 0.0015 |
| FG | 10 | 0.0014 | FT | 12 | 0.0004 |
| FH | 10 | 0.0011 | FU | 12 | 0.0006 |
| FK | 10 | 0.0027 | FX | 12 | 0.0004 |
| | Average | 0.0024 | | Average | 0.0009 |

[1]Carbon and silicon contents of alloys intended to be 0.33 per cent and 2 per cent, respectively. See Tables I and II for other elements.
[2]Weight loss in grams per sq. in. per day. Specimens were ⅜ inch diameter x 2 inch long cylinders. Scale was removed electrolytically in a fused-salt bath.

to oxidation than alloys with only 10 per cent chromium. However, when the silicon content is 2 per cent or higher, this difference is less pronounced. Increasing the silicon content from 1 to 2 per cent brings about a marked improvement in the resistance to oxidation. In some cases there is further improvement in resistance to oxidation on increasing the silicon to 3 to 4 per cent, but this generally results in loss of ductility. From observed losses in weight of alloys containing chromium in the range of 10 to 13 per cent and 2 per cent silicon or more, it is evident that the weight loss at 1600 degrees Fahr. (870 degrees Cent.) compares favorably with the average weight loss of the "HH" type alloys at 2000 degrees Fahr. (1095 degrees Cent.) where the average weight loss was 0.0151 grams per square inch per day. Many of the present alloys are definitely below this value. Resistance to oxidation at 1400 degrees Fahr. (760 degrees Cent.) is still better.

The 18-8 alloys as represented by DU are equal to the best of the new alloys in resistance to oxidation at 1400 and 1600 degrees Fahr. (760 and 870 degrees Cent.) and are superior to some of them. One alloy of the "HH" type included in this series of tests, DX, as would be expected, showed excellent resistance to oxidation.

Since all of the above tests have been made under conditions of continuous heating, tests were made on a series of alloys sub-

jected to cyclic heating. The results are shown in Table XV. The average weight loss under this condition is somewhat higher for the alloys of 10 per cent chromium than for those of 12 per cent, but in both cases the weight losses were relatively low, and results indicate that the scale formed on these alloys is adherent and does not chip off with change in temperature and cause excessive metal loss.

Thus the over-all picture of resistane of these alloys to oxidation at 1400 degrees Fahr. (760 degrees Cent.) and even at 1600 degrees Fahr. (870 degrees Cent.) is generally satisfactory if the silicon content is about 2 per cent or higher, and data in other parts of this paper show that 2 per cent of silicon can be used without significant loss in ductility.

### Corrosion Tests in Sulphur-Bearing Flue Gases

A limited amount of testing has been done on the corrosion resistance of the new alloys in sulphur-bearing flue gases, and comparisons are made between them and an 18-8 alloy and also between them and an alloy of the "HH" type. Tests have been made both at 1400 and 1600 degrees Fahr. (760 and 870 degrees Cent.). The results are given in Table XVI. The tests at 1600 degrees Fahr. (870 degrees Cent.) are under two conditions, one of which may be described as with excess oxygen and the other with incomplete combustion; the average compositions of the atmospheres are given in Table XVI. In both of these cases, the sulphur content would be considered much above normal expectation, i.e., it would be rated as an excessive amount of sulphur. Under Test A, there was a substantial difference depending upon the chromium content, and the alloys of 12 to 13 per cent chromium were definitely superior to those of 10 per cent chromium. The 18-8 alloy was not tested under this condition. One alloy of the "HH" type was tested and found markedly superior to the best of the new alloys.

Under the conditions of Test B, that is, incomplete combustion, the advantage of the higher chromium content was less evident. The 18-8 alloy was somewhat better than the best of the new alloys tested, and an alloy of the "HH" type was markedly superior to any of the new alloys or to 18-8.

Under the conditions of Test C at 1400 degrees Fahr. (760 degrees Cent.), in which the sulphur content was of the order encountered in a more normal gas atmosphere, the alloys show quite

**Table XVI**

**Corrosion Behavior of Alloy Materials in Flue Gas Atmospheres**

| Alloy No. | Composition—Per Cent Cr | Ni | Mn | Si | Exposure Temp.—1600 Degrees Fahr. Time—100 Hours Test A* 220 Grains S Per 100 Cu. Ft. Excess Oxygen Weight Loss—Grams Per Sq. In. Per Day | Test B* 200 Grains S Per 100 Cu. Ft. Incomplete Combustion Weight Loss—Grams Per Sq. In. Per Day | Exposure Temp.—1400 Degrees Fahr. Time—100 Hours Test C* 19 Grains S Per 100 Cu. Ft. Conditions of Incomplete Combustion Weight Loss—Grams Per Sq. In. Per Day | Test D* 104 Grains S Per 100 Cu. Ft. Weight Loss—Grams Per Sq. In. Per Day |
|---|---|---|---|---|---|---|---|---|
| FB | 10 | 6 | 7 | 2 | ..... | ..... | ..... | ..... |
| FC | 10 | 6 | 8 | 2 | 0.193 | ..... | ..... | 0.0080 |
| GA | 9.9 | 7.1 | 6.0 | 2.6 | ..... | ..... | ..... | 0.0717 |
| GC | 10 | 8 | 3 | 2 | 0.179 | 0.302 | 0.00063 | ..... |
| FH | 10 | 8 | 5 | 2 | 0.205 | 0.273 | ..... | ..... |
| FI | 10 | 8 | 6 | 2 | ..... | ..... | 0.00170 | 0.0115 |
| FK | 10 | 8 | 8 | 2 | 0.158 | ..... | ..... | ..... |
| FO | 12 | 6 | 7 | 2 | ..... | ..... | ..... | 0.0333 |
| GF | 12 | 8 | 3 | 2 | 0.099 | ..... | 0.00047 | 0.0117 |
| FV | 12 | 8 | 5 | 2 | 0.032 | 0.214 | ..... | ..... |
| FW | 12 | 8 | 6 | 2 | ..... | 0.158 | 0.00160 | ..... |
| FX | 12 | 8 | 8 | 2 | 0.063 | ..... | ..... | 0.0113 |
| GBA | 13 | 9 | 9 | 1.5 | 0.034 | ..... | ..... | 0.0112; 0.0089 |
| DU | 18 | 8 | 1 | 1 | ..... | 0.110 | 0.00064 | 0.0183; 0.0106 |
| AF | 25.2 | 11.4 | 0.87 | 1.5 | 0.0023 | ..... | 0.00057 | 0.0019 |
| AG | 25.5 | 12.5 | 0.78 | 1.1 | ..... | 0.008 | ..... | ..... |

*Average Composition of Gas Atmospheres Used

| | Per Cent by Volume $CO_2$ | $O_2$ | CO | $H_2$ | $H_2O$ | S | N | Conditions Represented |
|---|---|---|---|---|---|---|---|---|
| Test A | 12.4 | 8.0 | ... | ... | 4.6 | 220 grains | bal. | Excess air over that for complete combustion. Excessively high sulphur content. |
| Test B | 5.9 | 0.0 | 4.8 | 3.5 | 4.0 | 200 grains | bal. | Deficiency of air for complete combustion. Excessively high sulphur content. |
| Test C | 7.0 | 0.0 | 6.4 | 5.1 | 3.8 | 19 grains | bal. | Deficiency of air for complete combustion. Low sulphur content. |
| Test D | 9.0 | 0.0 | 5.5 | 4.7 | 5.1 | 104 grains | bal. | Deficiency of air for complete combustion. Moderately high sulphur content. |

small losses. Alloy DU (18-8) is within the range covered by the new alloys, and this was true of the higher chromium-nickel alloys of the "HH" type represented by AF. Thus it is indicated that the new alloys at 1400 degrees Fahr. (760 degrees Cent.), in an atmosphere of low sulphur content, compare favorably with 18-8 and not unfavorably with the 25 per cent chromium - 12 per cent nickel type tested at the same temperature. Increasing the sulphur content to 104 grains per 100 cubic feet had the general effect of increasing the amount of weight loss. Again it is found that the best of the new alloys are equivalent to 18-8 but not equivalent to the "HH" type at the same temperature.

Thus the general indications are that the resistance to corrosion of these alloys is quite good at 1400 degrees Fahr. (760 degrees Cent.), especially if the sulphur content is low. The corrosion attack increases as the sulphur content increases, but this is found to be true for the 18-8 type and for the "HH" type as is shown in the tabulated data. At 1600 degrees Fahr. (870 degrees Cent.) with relatively high sulphur content, corrosion attack is markedly increased, and the alloys appear to be somewhat inferior to 18-8 and decidedly inferior to the "HH" type under the conditions of excess oxygen or incomplete combustion. It seems likely, however, that the corrosion resistance of the new alloys at 1400 degrees Fahr. (760 degrees Cent.) is at least as good as that of the "HH" type at 1800 degrees Fahr. (980 degrees Cent.).

## Nitrogen Content of Alloys

In the general procedure used in making the alloys studied, no nitrogen was intentionally added. However, in the case of one heat of the composition represented by GK, nitrogen was intentionally added.

Alloys of 8 per cent nickel from the F and G series with chromium contents of 10 to 12 per cent were analyzed for nitrogen content and then their properties were studied to determine if the variations in nitrogen had any noticeable effect. Table XVII gives the laboratory numbers and the chromium and nitrogen contents of these alloys. Only in the case of Alloy GK was there intentional addition, where it was intended to produce an alloy of about 0.08 per cent nitrogen. The fact that the nitrogen content of this alloy was only 0.05 per cent and close to the average of the range of 0.04

to 0.08 per cent with an average of 0.06 per cent suggests that these alloys do not take up large amounts of nitrogen.

There is no evident relation between chromium content and nitrogen content or between manganese content and nitrogen content. In fact, there is no evident relation between chemical composition, in the range studied, and nitrogen content.

A study has been made of the tensile properties of the alloys listed in Table XVII to see if there could be found any relation to

**Table XVII**
**Nitrogen Contents of Alloys**

| Lab. No. | Cr Per Cent | N Per Cent | Lab. No. | Cr Per Cent | N Per Cent |
|---|---|---|---|---|---|
| FH | 9.8 | 0.04 | GF | 12.0 | 0.06 |
| FI | 10.3 | 0.04 | GC | 10.0 | 0.05 |
| FJ | 10.0 | 0.05 | GK* | 12.3 | 0.05 |
| FK | 10.0 | 0.08 | GN | 11.0 | 0.08 |
| FV | 12.0 | 0.06 | GO | 11.0 | 0.08 |
| FX | 11.4 | 0.06 | | | |
| FX-1 | 11.9 | 0.04 | | | |
| FW | 12.0 | 0.08 | | | |

Range 0.04 to 0.08 Per Cent N
Average 0.06 Per Cent N

*Added nitrogen by using high-nitrogen ferrochromium.

nitrogen content. No significant relations were found, so it is considered that, in the range of nitrogen studied (0.04 to 0.08 per cent), it is without significant effect on the properties of these alloys, and it is also indicated that these alloys will not, under the melting practice used, have large nitrogen contents.

## Thermal Expansion and Density of Alloys

Thermal expansion data have been obtained for seven alloys. One alloy, EC, is highly ferritic in the "as-cast" condition; a second alloy, EP, is partially ferritic; while five other alloys, FH-1, GE, FX-1, GJ, and GB, are substantially austenitic.

The coefficients of expansion of the alloys were determined for the temperature range from 75 to 1700 degrees Fahr. (925 degrees Cent.). All of the specimens were in the "as-cast" condition at start of the test. The heating and cooling rate used in testing was 5 degrees Fahr. per minute. A brief summary of the linear expansion data is given in Table XVIII, which also gives the compositions of the alloys studied. From the data in Table XVIII, it is shown that the expansion of the ferritic alloy EC is considerably less than for

the austenitic composition, while Alloy EP, which is partially ferritic after 24 hours' exposure at 1400 degrees Fahr. (760 degrees Cent.) (magnetic permeability 1.12), expands moderately less than the austenitic alloys. Alloys EC and EP both showed a small increase in length as a result of the heat treatment received in testing. This most likely is caused by an increase in amount of ferrite as the austenite to ferrite transformation is accompanied by expansion.

For comparison purposes, thermal expansion data for an alloy of the "HH" type are included in Table XVIII. It is evident that the coefficient of thermal expansion for the new alloys is close to that of the "HH" type but slightly greater. The linear expansion of the new alloys over the range of 75 to 1700 degrees Fahr. (925 degrees Cent.) is slightly greater, 1.78 to 1.85 per cent as compared with 1.71 per cent for the "HH" type alloys.

## Density Determinations

The density has been determined for twenty specimens of the new materials. For this work, specimens which had been prepared for the high temperature corrosion work were used. Since the specimens had been accurately weighed and measured for the corrosion test work, the density measurements entailed only the calculation of the weight per unit volume.

The average density value for twenty determinations was 7.70 grams per cubic centimeter, or 0.278 pounds per cubic inch. The alloys were within the following composition range:

| Cr | Ni | Mn | Si | C |
|---|---|---|---|---|
| 10-13 | 6-10 | 5-9 | 2 | 0.33 |

The values calculated for the individual samples varied about $\pm 0.04$ grams per cubic centimeter from the reported average value. The density of these alloys is quite close to that of the "HH" type alloy for which previous work had shown a value of 7.73 grams per cubic centimeter or 0.279 pounds per cubic inch.

## Melting Practices

The melting practices used in producing the alloys in this study have been discussed. However, some special work was done on the use of silico-manganese in place of the ferro-alloys, and some attention has been given to the nitrogen content of these alloys and the effect of nitrogen on their properties.

**Table XVIII**
**Linear Coefficients of Expansion of Ferritic, Partially Ferritic, and Austenitic Alloys**

| Alloy No. | Composition—Per Cent | | | | | Average Linear Coefficient of Expansion Degrees Fahr. from | | | Per Cent Linear Expansion |
|---|---|---|---|---|---|---|---|---|---|
| | Cr | Ni | Mn | Si | C | 75 to 200° F. | 75 to 1400° F. | 75 to 1700° F. | 75 to 1700° F. |
| | | | | | (Ferritic Alloy) | | | | |
| EC† | 12 | ... | 0.5 | 2 | 0.30 | 5.9 x $10^{-6}$ | 7.2 x $10^{-6}$ | 7.4 x $10^{-6}$ | 1.15 |
| | | | | | (Partially Ferritic Alloy) | | | | |
| EP | 12 | 6 | 4 | 2 | 0.50 | 9.4 x $10^{-6}$ | 10.9 x $10^{-6}$ | 11 x $10^{-6}$ | 1.78 |
| | | | | | (Austenitic Alloys) | | | | |
| FH-1 | 9.8 | 8.1 | 5.3 | 2.04 | 0.32 | 10.3 x $10^{-6}$ | 11.2 x $10^{-6}$ | 11.3 x $10^{-6}$ | 1.84 |
| GE | 10 | 9 | 5 | 2 | 0.33 | 10.2 x $10^{-6}$ | 11.2 x $10^{-6}$ | 11.4 x $10^{-6}$ | 1.85 |
| FX-1 | 11.9 | 8.1 | 8.0 | 2.02 | 0.32 | 9.9 x $10^{-6}$ | 11.2 x $10^{-6}$ | 11.15 x $10^{-6}$ | 1.81 |
| GJ | 12 | 10 | 5 | 2 | 0.33 | 10.1 x $10^{-6}$ | 11.35 x $10^{-6}$ | 11.4 x $10^{-6}$ | 1.85 |
| GB | 13 | 9 | 9 | 1.5 | 0.30 | 10.15 x $10^{-6}$ | 11.4 x $10^{-6}$ | 11.4 x $10^{-6}$ | 1.85 |
| "HH" Type* | 25 | 12 | 0.9 | 1 | 0.40 | 8.0 x $10^{-6}$ | 10.1 x $10^{-6}$ | 10.5 x $10^{-6}$ | 1.71 |

†Also contains 0.5 per cent Mo.
*Average values from earlier researches.

There is known to have been some commercial plant experience with alloys of the type described in this paper, and it is to be hoped that plant metallurgists who have had experience in producing such alloys will discuss this paper. It is anticipated that some trouble may be encountered in manganese recovery in acid arc furnaces, but it is understood that chromium recovery is improved so that loss of manganese is, at least in part, compensated by reduced loss of chromium.

*Silico-Manganese vs. Ferro-Manganese and Ferro-Silicon for Adding Manganese and Silicon*—Alloys FE-1, FH-1, and FX-1 were made using silico-manganese instead of ferro-silicon and ferro-manganese, and were intended to duplicate Alloys FE-1, FH, and FX, which had been made earlier using ferro-silicon and ferro-manganese.

Table XIX gives the compositions, as determined by chemical analyses, and tension test results for room temperature and for 1400 degrees Fahr. (760 degrees Cent.).

The heats made using silico-manganese show better room temperature strength and ductility properties than those made using the ferro-alloys. At 1400 degrees Fahr. (760 degrees Cent.) the alloys are more closely similar in properties. No definite reason can be given for the slight superiority of the silico-manganese heats. The important point is that silico-manganese can be used instead of the ferro-alloys and a saving in cost will result. Bend tests on the alloys made with silico-manganese using specimens as cast, aged 24 hours at 1400 degrees Fahr. (760 degrees Cent.), 24 hours at 1200 degrees Fahr. (650 degrees Cent.), and 500 hours at 1200 degrees Fahr. (650 degrees Cent.) showed that their properties were as good as those of the alloys made with the ferro-alloys.

One point on melting procedure which may be a factor in the poorer properties of the ferro-alloy heats FE, FH, and FX is that, for these heats, the ferro-manganese was added and melted along with the ferro-chromium and the ferro-silicon added later when the heat was fully molten and close to pouring temperature, while in making the silico-manganese heats this alloy was added shortly before pouring.

The early addition of manganese resulted in some loss of this element, while practically complete recovery of manganese was obtained when using silico-manganese.

In the case of Heat GK, both the ferro-silicon and the ferro-

**Table XIX**

**Comparison of Tensile Properties of Alloys Made Using Ferro-Manganese and Ferro-Silicon with Those Made Using Silico-Manganese[1]**

| Addition Alloy | Alloy No.[3] | Composition—Per Cent | | | | | At Room Temperature | | | | At 1400 Degrees Fahr. | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Cr | Ni | Mn | Si | C | Tensile Strength | Yield Str. (0.2% Def.) | Elong. in 2″ | Red. of Area | Tensile Strength | Yield Str. (0.2% Def.) | Elong. in 2″ | Red. of Area |
| | | | | | | | Psi. | | Per Cent | | Psi. | | Per Cent | |
| FeSi + FeMn | FE | 10.2 | 6.9 | 5.6 | 2.07 | 0.32 | 67,800 | 41,000 | 7.0 | 8.9 | 25,600 | 18,500 | 25.0 | 33.4 |
| SiMn | FE-1 | 10.0 | 7.0 | 6.1 | 1.97 | 0.32 | 92,300 | 47,400 | 14.0 | 16.0 | 28,200 | 21,400 | 22.0 | 39.8 |
| FeSi + FeMn | FH | 9.5 | 7.6 | 4.6 | 1.92 | 0.32 | 81,500 | 38,800 | 15.5 | 17.9 | 23,400 | 18,500 | 19.0 | 20.9 |
| SiMn | FH-1 | 9.8 | 8.1 | 5.3 | 2.04 | 0.32 | 101,100 | 43,400 | 27.0 | 23.2 | 27,200 | 19,900 | 22.0 | 28.2 |
| FeSi + FeMn | FX | 11.4 | 7.9 | 6.7 | 1.77 | 0.32 | 92,700 | 41,800 | 20.0 | 21.6 | 29,800 | ..... | 20.0 | 30.8 |
| FeSi + FeMn | GK[2] | 12.3 | 7.8 | 7.8 | 2.28 | 0.35 | 91,200 | 43,100 | 19.0 | 23.4 | 28,000 | 19,500 | 24.5 | 35.7 |
| SiMn | FX-1 | 11.9 | 8.1 | 8.0 | 2.02 | 0.32 | 98,500 | ..... | 23.0 | 22.3 | 28,400 | 20,700 | 18.0 | 24.1 |

[1]All bars tested had been aged 24 hours at 1400 degrees Fahr. prior to test.
[2]The test bars of Alloy GK were from a 100 lb. heat, all others were from 15 lb. heats.
[3]Heats FE, FH and FX had the ferro-silicon and ferro-manganese added earlier in the heat than for the other alloys, and it is believed that this accounts for their lower manganese recovery; the intended manganese contents being FE—6 per cent, FH—5 per cent, FX—8 per cent.

manganese were added when the heat was fully molten and near the pouring temperature. The recovery of manganese in this instance was nearly as good as when silico-manganese was used.

## Summary and Conclusions

An emergency type of alloy to be used at temperatures up to and including 1400 degrees Fahr. (760 degrees Cent.) has been developed. By using alloys with chromium contents in the range of about 10 to 12 per cent with the chromium supplemented by about 2 per cent of silicon, with the nickel and manganese balanced so as to produce wholly austenitic alloys, and with carbon contents in the range of about 0.30 to 0.35 per cent, promising alloys are produced. Certainly alloys have been developed which meet the requirements, set forth in the introduction to this paper, which the Alloy Casting Institute considered most essential.

The alloys, when of the preferred composition, have adequate toughness for handling in the foundry and are low enough in hardness to be machinable. They do not develop excessive hardness or show marked loss in ductility on aging at the proposed service temperature of 1400 degrees Fahr. (760 degrees Cent.) or at intermediate temperatures. The strengths of the alloys of preferred composition are relatively high at room temperature and at 1400 degrees Fahr. (760 degrees Cent.) and are substantially higher than extensively used heat resisting alloys at 1800 degrees Fahr. (980 degrees Cent.). The load-carrying capacities of the new alloys as determined by creep tests at 1400 degrees Fahr. (760 degrees Cent.) compare very favorably with published data for alloys of the "HH" type at 1800 degrees Fahr. (980 degrees Cent.).

The structures of the alloys and the structural stability of the alloys have been determined. By properly balancing the composition, the alloys can be made so stably austenitic that they remain so under all of the conditions of testing which have been applied. As the alloys depart from the stably austenitic condition, they lose slightly in load-carrying capacity and structural stability, but it is indicated that they may depart somewhat from the stably austenitic composition without serious loss in load-carrying capacity or in ductility. However, in extreme departures from the limiting compositions of nickel and manganese for a given chromium level, the alloys become strongly ferritic, have reduced load-carrying capacities, and in some cases, show marked loss in ductility on aging.

Balancing the amount of nickel and manganese against the chromium content seems to be the most important requirement for wholly austenitic alloys, and it is significant that the amount of nickel and/or manganese required for a wholly austenitic alloy increases as the chromium content decreases in the range of 15 to 10 per cent. While most of the work has been done on alloys with a maximum of about 12 per cent chromium, this value is not a technical maximum but rather a strategic one, and there appears to be no technical difficulty in using alloys containing up to 15 per cent chromium. Corrosion resistance would be improved by increasing the chromium content from 12 to 15 per cent. Carbon within the range of 0.30 to 0.50 per cent seems to have relatively little effect on whether or not the alloys will be wholly austenitic, but as the carbon content increases over this range, the ductility of the alloys decreases. A preferred carbon content seems to be in the range of 0.30 to 0.35 per cent.

A preferred silicon content seems to be 2 per cent because the corrosion resistance is materially improved by increasing the silicon content from 1 to 2 per cent, while if the silicon content is increased from 2 to 3 per cent, there is some loss in ductility. The nitrogen content found in the alloys which have been analyzed varied over the narrow range from 0.04 to 0.08 per cent. No important effect was found to be associated with this variation in nitrogen content. All of the alloys have been made with melting stock low in sulphur and phosphorus, and the effects of larger amounts of these elements have not been studied.

The coefficient of thermal expansion for these alloys which are wholly austenitic is only slightly greater than that for the "HH" type of alloy, and the density is only slightly less than that of the "HH" type. Some comparisons have been made between alloys containing about 6 per cent chromium and the new alloys, and likewise, some comparisons have been made between an alloy of the 18-8 type and the new alloys. The 6 per cent chromium alloys appear to be inferior in practically all respects. On the other hand, the 18-8 alloys are equal in many respects and superior in some but require a substantially greater amount of scarce alloying metals. One brittle failure in an 18-8 alloy in creep test has been encountered, and it is suggested that further work is needed on that type of alloy to see if brittle failure under substantial deformation in creep testing is a characteristic.

The new alloys contain chromium in the range of 10 to 13 per

cent, nickel 4 to 10 per cent, manganese 2 to 12 per cent, silicon about 2 per cent, and carbon about 0.30 to 0.35 per cent. A better range would seem to be nickel 6 to 9 per cent with enough manganese to make the alloy wholly austenitic.

## Acknowledgments

The authors are glad to acknowledge the sponsorship for the research work on which this paper is based of the Alloy Casting Institute of which E. A. Schoefer, 39 Broadway, New York City, is Executive Secretary; W. H. Worrilow, Lebanon Steel Foundry, President; F. B. Foley, The Midvale Company, Chariman of the Technical Research Committee; and L. E. Welch, The Ohio Steel Foundry, Chairman of the High Temperature Committee.

They are also glad to acknowledge the assistance of members of the Battelle staff, including Howard C. Cross and Ward Simmons for the creep tests, C. T. Greenidge and Harvey Priest for assistance in melting and casting, and Dean D. Burgan, Anton DeSales Brasunas, and David Goldberg for assistance in other phases of the research program.

## Appendix

Since this paper was written, some additional work has been done, and it is considered desirable to present the more important new data.

The load on Alloy GS was increased from 4000 to 7000 pounds per square inch and run for 467 hours at the higher load; similarly, the load on Alloy GH-2 was increased from 4000 to 6000 pounds per square inch and run for 648 hours; Alloy FV-2 was run 479 hours at 4000 pounds per square inch and then 835 hours at 6000 pounds per square inch; and Alloy FQ-2 was run 599 hours at 4000 pounds per square inch and 939 hours at 6000 pounds per square inch. The curves for these tests are shown in Fig. 16.

From the data in Table X and the data shown on the curves of Fig. 16, it is possible to estimate the loads for the various alloys to give a minimum creep rate of 0.0001 per cent per hour (L.C.S. values), and it is indicated that these values will range from 7000 to 4000 pounds per square inch at 1400 degrees Fahr. (760 degrees Cent.), with the high values found with stably austenitic alloys and

with lower values as the composition ranges to the marginal alloys with insufficient manganese or nickel. The L.C.S. values at 1600 degrees Fahr. (870 degrees Cent.) are less well defined, because of the limited number of tests, but are indicated to be in the range of

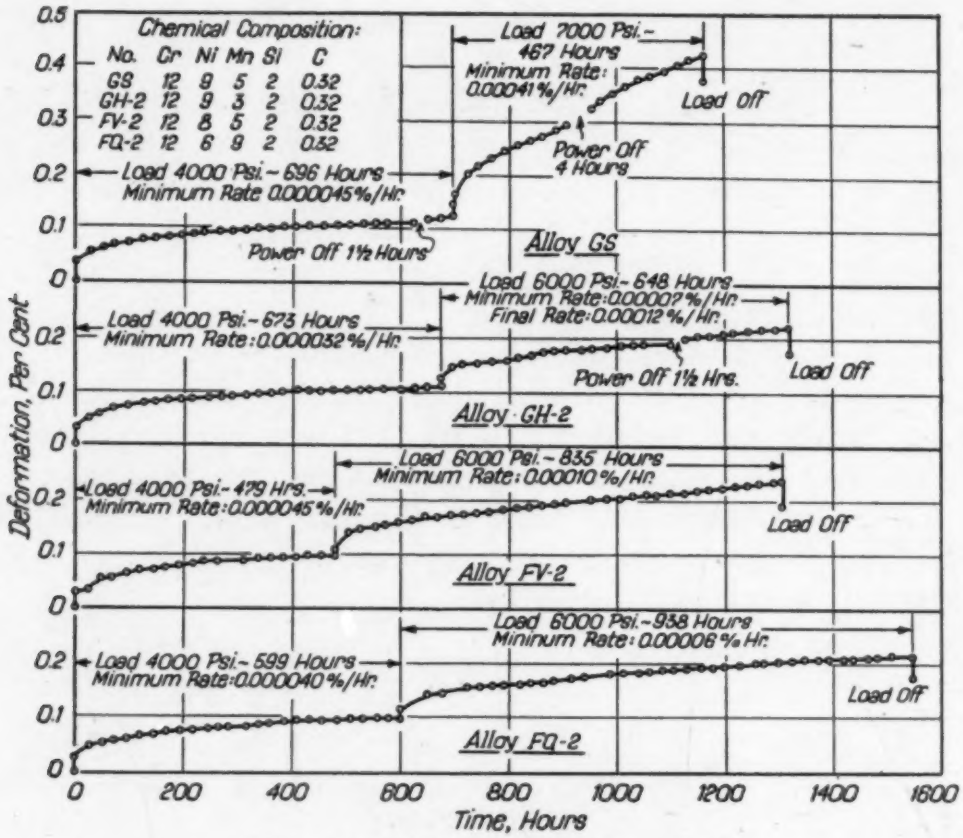


Fig. 16—Creep Tests at 1400 Degrees Fahr.

about 3000 to 1500 pounds per square inch, again varying with the composition.

An additional test has been run on Alloy DU-2 (18-8) at 1600 degrees Fahr. (870 degrees Cent.) under a load of 5000 pounds per square inch, and it broke with a brittle fracture after 172 hours.

The specimens which had been tested in creep were tested in tension at room temperature to determine their residual ductility. The results are given in Table XX. This table gives the chemical compositions of the alloys, the creep testing conditions, the elongation values for specimens which had been subjected to creep testing, and, for comparison purposes, values for specimens which had not been creep tested. Data are also quoted for two alloys of the "HH" type (25 per cent chromium-12 per cent nickel) for comparison.

**Table XX**
**Ductility After Creep Testing**

| Alloy No. | Composition—Per Cent C | Cr | Ni | Mn | Si | Creep Testing Conditions Temp. °F. | Load—Psi. | Time Hrs. | Elongation[1] Per Cent in 2 Inches | Elongation[2] Per Cent in 2 Inches |
|---|---|---|---|---|---|---|---|---|---|---|
| GS | 0.32 | 11.8 | 8.8 | 4.7 | 2.2 | 1400 | 4000–7000 | 1162 | 8.0 | .... |
| GH-2 | 0.32 | 11.7 | 8.9 | 3.2 | 2.2 | 1400 | 4000–6000 | 1321 | 6.0 | 16.5 |
| FV-2 | 0.34 | 11.7 | 7.9 | 5.3 | 2.3 | 1400 | 4000–6000 | 1314 | 4.0 | 13.0 |
| FQ-2 | 0.32 | 11.6 | 5.8 | 8.3 | 2.1 | 1400 | 4000–6000 | 1537 | 8.0 | 10.5 |
| GK | 0.35 | 12.3 | 7.8 | 7.8 | 2.28 | 1400 | 4000–5000–7000 | 1703 | 6.5 | 19.0 |
| FE-1 | 0.32 | 10.0 | 7.0 | 6.1 | 1.96 | 1400 | 4000–6000 | 1790 | 21.5 | 14.0 |
| DU-2 | .... | 18.0 | 8.0 | 1.0 | 1.00 | 1400 | 7000 | 1012 | 20.0 | 25.5 |
| GK | 0.35 | 12.3 | 7.8 | 7.8 | 2.28 | 1600 | 2500–3000 | 1136 | 7.0 | 19.0 |
| FH-2 | 0.32 | 9.8 | 7.8 | 5.1 | 2.2 | 1600 | 2000 | 552 | 12.0 | 15.5 |
| "HH" Alloy[3] | 0.32 | 25.9 | 11.5 | 0.46 | 0.45 | 1400 | 6000 | 1150 | 3.0 | 6.8 |
| "HH" Alloy[3] | 0.29 | 26.3 | 11.5 | 0.53 | 1.56 | 1400 | 4000 | 1033 | 2.0 | 19.8 |

[1]Tested at room temperature after creep testing.
[2]Tested at room temperature after aging 24 hours at 1400 degrees Fahr.
[3]Data from Avery, Cook, and Fellows.

It will be evident that the new alloys compare favorably with the "HH" type as to retention of ductility on being subjected to stress at elevated temperature. It is to be noted that the 18-8 alloy (DU-2) also showed good retained ductility after creep testing at 1400 degrees Fahr. (760 degrees Cent.). However, the 18-8 specimens tested at 1600 degrees Fahr. (870 degrees Cent.) broke with a brittle fracture, whereas the new alloys had good ductility after being tested in creep at that temperature.

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## DISCUSSION

**Written Discussion:** By W. F. Furman, vice-president, and E. M. Anger, plant metallurgist, The Duraloy Co., Scottdale, Pa.

As producers of high alloy heat resistant castings, we are extremely interested in the very thorough investigations described by Dr. Harder and Mr. Gow. The need for an intermediate alloy, for operating temperatures below 1400 degrees Fahr. (760 degrees Cent.) but above temperatures at which alloyed cast iron can be satisfactorily used, has long been recognized. The chromium, nickel, manganese alloy developed at Battelle apparently meets this, and also the necessity for conserving during the war the scarce elements, nickel and chromium.

During normal times the cry of the user for such an intermediate temperature alloy is combined with the requirement that it must also be intermediate in price. The standard high temperature alloys, such as 24 per cent chromium, 12 per cent nickel, can ordinarily be used with satisfactory results at these intermediate temperatures, but their comparatively high cost often deters their use.

Unfortunately, the alloy described in this paper does not meet this requirement. While the actual cost of alloying elements in it does not quite equal the total cost of the elements in an alloy such as HH, 24 per cent chromium, 12 per cent nickel, the difference is slight; and other cost factors such as melting, molding and cleaning would be the same. This would mean that the selling prices for castings would be approximately the same for both alloys, so there would be no practical inducement for substituting the lower grade alloy.

It might be interesting to compare results secured on a heat recently run at The Duraloy Company with those shown in this paper. The heat in question was produced in a small arc type electric basic furnace, which is used for commercial heats. The heat was about four hundred pounds, and analyzed as follows:

| C | Si | Mn | Cr | Ni |
|---|---|---|---|---|
| 0.40 | 2.61 | 9.45 | 12.10 | 5.87 |

This analysis compares closely with the 10 to 13 per cent chromium, 6 to 9 per cent manganese, 2 per cent silicon, 4 to 10 per cent nickel, 0.30 to 0.35 per cent carbon listed in the paper.

It was found that the same furnace practice used for a standard 18-8 alloy could be followed. The heat was poured at a slightly lower temperature than is ordinarily used for 18-8, but was very fluid and seemed to have the property of solidifying very quickly from the liquid condition. It has less cutting action on the sand than 18-8 and castings were smoother. It is apparent that the alloy could be run into comparatively thin sections.

Because of the lower pouring temperatures there was very little burned on sand, so that there would be no particular cleaning room problem. In this particular heat the shrinkage appeared to be about 9/32 inch to the foot. The heat was poured into commercial molds, and also a number of test coupons were made.

Physical properties as cast were as follows:

| U.T.S. p.s.i. | Y.S. p.s.i. | Per cent Elongation 2 inches | Per cent Reduction in Area | B.H.N. |
|---|---|---|---|---|
| 91,300 | 55,000 | 21.0 | 20.2 | 187 |

Short time tests were run at 1400 degrees Fahr. (760 degrees Cent.) with the following results:

| U.T.S. p.s.i. | Per cent Elongation 2 inches | Per cent Reduction in Area |
|---|---|---|
| 43,200 | 9.5 | 15.2 |

Physical properties after aging at 1400 degrees Fahr. (760 degrees Cent.) for twenty-four hours were as follows:

| | U.T.S. | Y.S. | Per cent Elongation 2 inches | Per cent Reduction in Area |
|---|---|---|---|---|
| At room temperature | 105,200 | 58,000 | 10.0 | 12.6 |
| At 1400 degrees Fahr. | 35,000 | | 12.0 | 20.2 |

Samples were water-quenched after soaking at 1950 degrees Fahr. (1065 degrees Cent.), and physical properties were obtained as follows:

| U.T.S. | Y.S. | Per cent Elongation 2 inches | Per cent Reduction in Area |
|---|---|---|---|
| 108,500 | 54,700 | 39.0 | 28.8 |

A specimen in the as-cast condition was given a bend test, and reached almost a full bend before breaking.

In general it can be said that from the foundry standpoint this seems to be an entirely satisfactory composition, from which sound castings can be made without any particular foundry difficulties.

As an emergency alloy, for use during the war, with the particular object of conserving chromium and nickel, it is entirely adequate.

**Written Discussion:** By L. E. Welch, Ohio Steel Foundry Co., Springfield, Ohio.

The emergency type heat resisting alloy, which has been developed at Battelle Memorial Institute as part of the research program of the Alloy Casting Institute, fills the need of Industry for a suitable alloy for application at temperatures up to 1400 degrees Fahr. (760 degrees Cent.).

While this particular research program was born from an idea to conserve nickel and chromium, it nevertheless fits in with the Alloy Casting Institute's aim to propose and develop new types of heat and corrosion resisting alloys and to make improvements in the existing types.

The sixth requirement for an emergency alloy, as listed in the Introduction of this paper, states that the alloy should not present special foundry problems in melting or in casting. To the foundry, this is of primary consideration because no alloy or material has merit if it cannot be produced.

The test for ductility carried out by Battelle Memorial Institute, which consisted of pouring strip castings in each heat and then determining the amount of bend each of these castings would take, was intended to show one phase of the suitability of these alloys for foundry production.

Irregular and uneven metal sections tend to warp the castings so that it becomes necessary to straighten them. Alloys which will not take at least a 10-degree bend would be difficult to handle in the foundry. It is for this reason

that the Alloy Casting Institute has specified that the alloy be of such a character that the castings will take a reasonable amount of bending. You will note that the fully austenitic emergency manganese, chromium, nickel alloys will take a full bend in the as-cast condition and at least a 20-degree bend after aging at 1400 degrees Fahr. (760 degrees Cent.) for 24 hours.

Members of the Alloy Casting Institute were interested:

First—Whether or not the manganese could be satisfactorily added to heats made in the acid lined direct furnace (arc).

Second—Whether or not the resulting liquid metal would have sufficient fluidity to pour castings of various wall thicknesses.

Third—If heats of the emergency alloy made in commercial quantities would have properties comparable to the properties shown in this paper.

In order to ascertain these facts, commercial size heats of the emergency type alloys were made in the foundry with which I am connected and several types and design of castings were poured. The castings poured were intended for an experimental installation for one of our customers as well as for several low temperature draw furnaces in our heat treating department.

The heats made were all calculated to have about 6 per cent manganese and in all cases little difficulty was experienced in adding the manganese.

The manganese appeared to increase the fluidity of the metal to such an extent that it counteracted the natural loss of fluidity due to the loss of temperature of the molten metal because of the chilling action caused when the ferromanganese was added.

In order to cut down the manganese loss, the temperature of the molten metal should be kept as low as possible. The resulting castings produced will have a slightly wrinkled surface which does not interfere with the efficiency of the castings.

A few of the tests made on commercial heats of the emergency type heat resisting alloy gave the following data:

**Percentage Composition**

| Heat | C | Mn | Si | Ni | Cr |
|---|---|---|---|---|---|
| A | 0.33 | 4.88 | 1.17 | 8.77 | 14.45 |
| B | 0.34 | 6.68 | 2.57 | 8.45 | 12.80 |
| C | 0.32 | 6.00 | 2.19 | 6.18 | 14.20 |

**Physical Test Data**

| Heat | A | B | C |
|---|---|---|---|
| 1. Made on as cast specimens: | | | |
| Yield Strength PSI | 44500 | 52000 | 44500 |
| Tensile Strength PSI | 84500 | 89000 | 78000 |
| Per Cent Elongation in 2 inches | 30.0 | 23.5 | 17.0 |
| Brinell Hardness | 186 | 170 | 170 |
| 2. Specimens aged 24 hours at 1400 degrees Fahr. | | | |
| Yield Strength PSI | 42500 | 48000 | 46500 |
| Tensile Strength PSI | 97000 | 105000 | 80000 |
| Per Cent Elongation in 2 inches | 18.0 | 19.0 | 6.0 |
| Brinell Hardness | 197 | 217 | 229 |
| 3. Specimens aged 500 hours at 1400 degrees Fahr. | | | |
| Yield Strength PSI | 42000 | 44000 | 41000 |
| Tensile Strength PSI | 100000 | 92000 | 90000 |
| Per Cent Elongation in 2 inches | 15 | 10 | 9 |
| Brinell Hardness | 255 | 229 | 261 |

Magnetic tests on the specimens aged for 500 hours gave following results:

Heat A. Slightly magnetic on cold-worked end and very slightly on end of specimen not cold-worked.

Heat B. Nonmagnetic on both ends of specimen.

Heat C. Magnetic on cold-worked end of specimen—slightly magnetic on end of specimen not cold-worked.

The values shown by these tests fit in very well with Fig. 7 on page 434 of this paper. The curves in this figure indicate that:

Alloy A. Has just sufficient manganese, chromium and nickel to make it austenitic. The test after aging indicates it to be on the borderline for essentially austenitic alloy.

Alloy B. Was nonmagnetic on test which was to be inferred from the curve since this alloy has about 1 per cent more nickel than was needed to make the alloy essentially austenitic.

Alloy C. This alloy was the most magnetic of the three which was to be expected since there was not sufficient nickel to make the alloy essentially austenitic.

In conclusion will state that foundry indications are that this type of an emergency alloy can be satisfactorily produced and will meet the test results set forth in this paper.

**Written Discussion:** By C. K. Lockwood, Stainless Steel & Alloys Division, Shawinigan Chemicals Limited, Montreal, Canada.

The authors are to be congratulated again on an excellent piece of research. The knowledge that the foundry industry will have an alloy steel to take the place of the standard 25 per cent chromium-12 per cent nickel, should available supplies of chromium and nickel warrant it, is very comforting. It is perhaps unfortunate that the research did not point to a greater saving of nickel rather than chromium, but it appears that the nickel is necessary to produce a "wholly austenitic" alloy.

Some time ago we produced a heat of steel of high manganese content of the following composition:

| | Per Cent | | Per Cent |
|---|---|---|---|
| Carbon | 0.35 | Manganese | 7.52 |
| Chromium | 14.72 | Silicon | 2.72 |
| Nickel | 7.52 | | |

A test specimen was aged for 24 hours at 1400 degrees Fahr. (760 degrees Cent.). The tensile properties were as follows:

| | |
|---|---|
| Yield Strength | 56,125 pounds per square inch |
| Ultimate Strength | 86,525 pounds per square inch |
| Per Cent Elongation in 2 inches | 4 |

The value for elongation was disappointing but as this only represents one heat, not too much attention should be paid to the results. The test bar was cast from a standard keel block and not from the type of bar shown in Fig. 1. This may account partly for a lower elongation figure.

Castings produced in this heat were placed in service under conditions of cyclic heating from 1450 degrees Fahr. (790 degrees Cent.) to room temperature. An examination of the castings after some months service did not show any signs of deterioration.

We note that during the research on the "Emergency Alloy" both ferro-manganese and silico-manganese were used to produce suitable alloys. We were wondering if electrolytic manganese was tried, and if not, whether the authors would anticipate any difference in performance of an alloy produced with it.

**Written Discussion:** By Roger C. Sutton, director of engineering and metallurgy, General Alloys Co., Boston.

The work on the development of an alloy to conserve certain strategic material, and at the same time, to alleviate some of the hardships necessarily brought about by the War Production Board's Limitation Order No. M-21-g also sponsored by the Alloy Casting Institute and the result, this paper, is exceedingly comprehensive and well written. It is felt, however, that certain points should be brought clearly into focus.

Since the scope of the alloy developed is within the range of 1000 to 1400 degrees Fahr. (540 to 760 degrees Cent.) it is apparent from a study of the above mentioned Limitation Order that this emergency alloy can only replace the normal 5 per cent chromium steel or the heat resisting grade of 18 per cent chromium-8 per cent nickel. From a conservation standpoint, it is evident that it replaces only the 18-8 material unless the W.P.B. sees fit to relax their regulations to the degree permitting its use in place of the 5 per cent chromium steel. It is hoped that such action will be approved by that agency.

When used as a replacement for 18-8 alloy, a question arises as to just how much conservation is effected. It would appear that the sole saving in strategic materials has been the replacement of approximately 6 per cent of chrome, or in other words, one-third of the chrome used in the present accepted alloy, by the addition of some 7 per cent of manganese, or an increase of eight times in this element. Whether or not this is true conservation is a problem for the "watch-dogs" of our metallurgical stock piles. This is particularly important in view of the fact that the report shows the emergency alloy is no better than, and in most cases, slightly inferior to the normal 18-8 material. This latter statement, of course, is based entirely on the data presented in the paper since very little, if any, field experience has been accumulated. Since it normally requires at least one year of field service to prove the worth of heat resisting alloys and since one pound of alloy may well handle several hundred thousand pounds of heat-treated material, the receipt of such data will be of great interest.

The value of the creep tests and other mechanical property data given is questionable, particularly in view of the nature of the mechanism which would normally be fabricated and the temperature range over which such mechanism would logically operate. In general, creep test results are only indicative of the change in dimension under constant load at constant temperature, and are generally applicable where minute size changes have an importnt bearing on the function of the mechanism. Since all properly designed furnace mechanisms allow the necessary clearances, and since the effect of thermal expansion is somewhat greater dimensionally than size changes due to creep in stage No. 2 (assuming, of course, that the member in question has been properly stress analyzed), it is believed that this particular property is relatively unimportant. However, if we assume its importance, we still must consider the comparison of the results obtained on the emergency alloy with those obtained on the normal 18-8 material.

Fig. 12 shows an L.C.S. of just under 5000 pounds per square inch for alloy DU-2 setting 0.0001 per cent per hour as a minimum rate, when tested at 1600 degrees Fahr. (870 degrees Cent.), whereas Alloy GK shows an L.C.S. of slightly under 3000 pounds per square inch for the same minimum rate. It is to be noted that Alloy DU-2 broke during stage No. 2 of the creep test with a brittle fracture, and this may or may not be significant. The brittle fracture evidenced by Alloy DU-2 during stage No. 2 of the creep test at 1600 degrees Fahr. (870 degrees Cent.) is of little significance from a practicable standpoint since the Emergency Alloy use is limited to 1400 degrees Fahr. (760 degrees Cent.). Creep test run at 1400 degrees Fahr. (760 degrees Cent.) as shown in Fig. 11 also indicates considerable superiority as regards time deformation for the DU-2 alloy and in this case no unusual fracturing was evidenced. The entire picture, as mentioned above, points to a marked superiority of the 18-8 alloy, and in view of the relatively small saving in strategic materials, it is doubtful that the emergency alloy can economically justify itself.

Oxidation tests and corrosion tests with sulphur-bearing flue gas tend to bear out the above remarks. This discussion is in no way intended as a criticism of the aim or results of this investigation but merely as a caution to potential users.

It is not felt that it is a substitute for the 18-8 or higher alloy type of material as it is not thought that this alloy has anything unusual to offer on the basis of laboratory results. Unquestionably it is far superior to the 5 per cent chromium steels and may well be used as a replacement for them, W.P.B. permitting.

### Authors' Reply

These discussions add valuable additional information regarding the alloy. They are particularly valuable in that they represent plant production rather than laboratory production.

The alloy described by Messrs. Furman and Anger shows a composition which, on the basis of Fig. 7 of the paper, contains about 2 per cent more manganese than the minimum requirement for a wholly austenitic alloy. Thus, this alloy would approach the type referred to as "stably" austenitic, such as GK, in the paper. However, its silicon content is higher than the preferred value of about 2 per cent, and experience has shown that increasing the silicon tends to reduce the ductility. This effect is probably reflected in an elongation of only 10 per cent for the aged specimens. Their data suggest that this alloy may have its ductility improved by heat treatment. It is worth mentioning that this alloy is low in nickel (5.87 per cent) and high in manganese (9.45 per cent).

Of the alloys studied by Mr. Welch, A and B contained larger amounts of manganese or nickel than the minimum requirements for a wholly austenitic alloy. The excess on the basis of manganese is about 2 per cent, so that these alloys would approach the "stably" austenitic type. Alloy B, however, is somewhat high in silicon, and his data indicate that silicon tended to lower the ductility. His Alloy C is deficient in manganese or nickel and, on the basis of manganese content, is deficient to the extent of about 1.5 per cent manganese for a wholly austenitic alloy. It would, therefore, be a marginal alloy, and his results show that it was lower in ductility, both as-cast and after aging, than Alloys A and B, which are at least wholly austenitic.

The alloy reported by Mr. Lockwood, on the basis of the curves of Fig. 7 has approximately 2 per cent more manganese than the minimum requirement for a wholly austenitic alloy. This alloy, however, is somewhat high in silicon, 2.72 per cent, and doubtless the high silicon content tended to reduce the ductility. Mr. Lockwood's report that cyclic heating from 1450 degrees Fahr. (790 degrees Cent.) to room temperature over a period of some months did not show any signs of deterioration is highly interesting. No attempt has been made to use electrolytic manganese in the production of these alloys, but no difficulty would be anticipated. The economics, however, would be against the use of electrolytic manganese and apparently would favor the use of silico-manganese, which is now understood to be readily available.

Mr. Sutton's comments on the desirability of using precautions in introducing new alloys are evidently in order. It should be pointed out, however, that the rather extensive laboratory tests which have been made and the plant tests for which data now are available have not disclosed any characteristics of the alloys which indicate that they are not usable up to at least 1400 degrees Fahr. (760 degrees Cent.), and it is believed that they meet the requirements of the original specification for an emergency heat resistant alloy.

# INFLUENCE OF NICKEL, MOLYBDENUM, COBALT AND SILICON ON THE KINETICS AND Ar″ TEMPERATURES OF THE AUSTENITE TO MARTENSITE TRANSFORMATION IN STEELS

By H. H. Chiswik and A. B. Greninger

*Abstract*

*A study has been made of the individual effects of nickel, molybdenum, cobalt and silicon on the kinetics and the Ar″ temperatures of the martensite transformation in steels. Using the microscopic technique of differentiating between tempered (black) and non-tempered (white) martensite, the quantitative effect of each of the above alloying elements on the Ar″ temperature has been determined. Nickel (up to 15 per cent) was shown to decrease the Ar″ temperature of a 0.45 per cent carbon steel uniformly at a rate of about 19 degrees Cent. per 1 per cent nickel; molybdenum (up to 2 per cent) neither raised nor lowered the Ar″ temperatures of 0.50 per cent, 0.80 per cent, or 1.00 per cent carbon steels; similarly, silicon (up to 3.5 per cent) neither raised nor lowered the Ar″ temperatures of 0.72 - 0.84 per cent carbon steels; cobalt, however, in the range from 3.4 to 7.6 per cent, raised the Ar″ temperature of a 1.12 per cent carbon steel uniformly at a rate of about 19 degrees per 1 per cent cobalt.*

*None of these elements was found to alter in any way the kinetics of the austenite to martensite transformation as described by Greninger and Troiano for plain carbon steels; the martensite transformation remains independent of time also in the presence of these alloying elements, and proceeds only as the steel is cooled through the martensite range.*

THE isothermal decomposition of undercooled austenite in plain carbon steels has been shown by Davenport and Bain (1),[1] in their original S-curve work, to be characterized by two decomposi-

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

The experimental work of this paper was performed in the Laboratories of Physical Metallurgy of Harvard University.

A paper presented before the Twenty-fifth Annual Convention of the Society, held in Chicago, October 18 to 22, 1943. Of the authors, H. H. Chiswik is research metallurgist, Battelle Memorial Institute, Columbus, Ohio, and A. B. Greninger is associated with the metallurgical laboratory, University of Chicago. Manuscript received June 4, 1943.

tion rate maxima: one at about 550 degrees Cent. (1000 degrees Fahr.), the Ar′, the other below 250 to 300 degrees Cent. (575 degrees Fahr.), the Ar″. The second maximum decomposition rate is associated with the transformation of austenite to martensite. In a study of the kinetics of the austenite-martensite transformation in plain carbon steels Greninger and Troiano (2) have shown that this reaction proceeds at a very high and at present immeasurable rate, and that for all practical purposes it may be assumed to be independent of time. On the basis of these findings, the authors suggested that the martensite transformation as represented by the lower portion of the S-curve is in error. Griffiths, Pfeil and Allen (3), in their Second Report of the Alloy Steels Research Committee of the Iron and Steel Institute, have modified the S-curve to include these experimental facts, by drawing a line at the Ar″ temperature parallel to the time axis, to indicate that the reaction is independent of time. This mechanism of the kinetics of martensite formation in plain carbon steels has been recently verified by various other investigators, using different methods of analysis. Saunders and Kahles (4), using a photometric method, found that the amount of martensite present in a plain carbon steel of eutectoid composition (0.80 carbon, 0.64 manganese) quenched to some temperature below the Ar″ point depends only on the temperature interval between the Ar″ temperature and the temperature of the quenching bath. Furthermore, both Digges (5), (6) and Greninger (7) found that the Ar″ point in plain carbon steels and pure iron-carbon alloys is independent of the cooling rate, the latter using a cooling rate as high as 4000 degrees Cent. per second.

When alloying elements are dissolved in austenite, however, its subcritical isothermal transformation is affected in many and various ways, depending on the type and quantity of alloying element present. As was shown by Davenport (8), the transformation rate maximum at about 550 degrees Cent. (1000 degrees Fahr.) (the Ar′) is frequently replaced in alloy steels by two maxima. In many alloy steels there is a temperature range near 550 degrees Cent. (1000 degrees Fahr.) in which austenite is extremely stable (9), (10), this being particularly associated with the presence of chromium, tungsten, molybdenum or vanadium. A second region of comparative austenite stability often occurs around 300 degrees Cent. (575 degrees Fahr.). In view of these varied effects of alloying elements on the transformation of austenite at temperatures above the Ar″, it was thought

desirable to study their effects on the kinetics of the martensite transformation, in direct comparison with the mechanism outlined by Greninger and Troiano (2) for plain carbon steels. The present paper presents the experimental results of a study of the effects of nickel, molybdenum, cobalt, and silicon on the kinetics and location of the Ar″ points of the austenite to martensite transformation in steels.

## Materials, Preparation of Alloys and Experimental Technique

*Materials*—All the alloys used in this work were prepared by adding the desired amounts of each alloying element to one of the following commercial steels:

1) S.A.E. 1050 (0.51 carbon, 0.54 manganese, 0.19 silicon)
2) S.A.E. 1085 (0.89 carbon, 0.59 manganese, 0.23 silicon)
3) Hypereutectoid steel (1.08 carbon, 0.30 manganese, 0.12 silicon)
4) Commercial 1.3-1.35 per cent carbon drill rod steel.

In one case in the nickel series of alloys an S.A.E. 2350 steel was used directly; its analysis was: 0.47 carbon, 3.41 nickel, 0.60 manganese, and 0.23 silicon. The chief base materials were the two S.A.E. steels 1050 and 1085, as they are within a carbon content range that permits the gradual addition of alloying elements in considerable quantities without exceeding the austenite solubility limits. Since the aim in each alloy series has been to keep the carbon content constant, additions of carbon were necessary to make up for the diluting effect of the added alloying element. The carbon was added in the form of pure sugar charcoal. The resulting carbon content of some melts, however, due to inherent losses when melting in vacuo, varied from the intended composition by as much as 0.1 per cent. For this reason, whenever the amount of alloying element added was not sufficient to decrease the carbon content beyond this limit, no carbon was added at all.

Commercial steels were chosen for the base materials in preference to pure iron, in order to approximate as closely as possible commercial compositions with reference to their usual impurities, e.g., silicon, sulphur, phosphorus, etc., thus permitting a direct evaluation of each alloying element when compared with a commercial steel of the same carbon content.

The alloying elements were added in their pure form; their recorded analyses, as supplied by the manufacturer, were:

Nickel shot—Baker's Analyzed—0.01 copper, 0.002 lead, 0.01 cobalt, 0.01 zinc, 0.16 iron.

Cobalt strip—Baker's Analyzed—0.01 copper, 0.01 lead, 0.01 iron, 0.05 nickel

Silicon chips—commercial grade—impurities not stated.

Molybdenum wire—99.99+ per cent; impurities not stated.

The experimental ingots in their final form were analyzed for carbon and the added alloying element only. To ascertain to what extent the other alloying elements usually present in S.A.E. steels were affected by the melting operation, a small ingot of the S.A.E. 1085 steel was remelted without any alloying element additions, using the same melting practice, forging, homogenizing, and grinding technique as for the experimental alloy steel melts. The analysis of the remelted ingot was: 0.84 carbon, 0.05 manganese and 0.23 silicon, indicating a loss of 0.05 carbon, an almost total loss of the manganese (original content = 0.59 per cent), and no loss of silicon. To show that a similar loss of manganese occurred also in the preparation of the experimental alloy steels, two or three steels of each series were analyzed for manganese; the manganese content ranged from 0.05 to 0.09 per cent.

## Preparation of Alloys

The materials, 50 grams total, were melted together in a highly evacuated molybdenum wound resistance furnace, and kept in the molten condition for 5 to 10 minutes to ensure complete mixing and allow the escape of entrapped gases. The power was then shut off and the melt allowed to solidify in an alumina crucible under vacuum. The ingots were hot-forged at 1000 degrees Cent. (1830 degrees Fahr.) into ⅜-inch square bars, 3 to 4 inches long. These bars were given a homogenizing anneal of 48 hours at 1200 degrees Cent. in an inert atmosphere (purified nitrogen gas). ¼-inch specimens were cut from both ends and examined microscopically for cross-sectional uniformity. The ingot was also polished on one longitudinal side and etched deeply to reveal possible gross segregation. Ingots that showed any degree of microscopic non-uniformity along the longitudinal plane of polish were discarded, unless

the non-uniformity was confined to within ½ inch from either end, in which case the ends were cut off and discarded. The surfaces of the bars were then cleaned with a surface grinder until reduced to ¼ inch square.

### Preparation of Metallographic Specimens

All metallographic specimens were of uniform size, ¼ inch long and 0.039 to 0.040 inches in cross section[2]. A quarter inch cubic specimen of the hot-forged ingot yielded 25 slivers, when cut with a jeweler's saw in a special slotting jig. Thus, a half inch specimen cut from the center of the hot-forged bar, with a yield of 50 slivers, was more than sufficient for a complete investigation. Samples for chemical analysis were also taken from the center of the forged bar. Unfortunately, however, the use of the fine jeweler's saw was confined to the relatively soft alloys. Ingots with high alloying element contents had to be cut with a high speed steel blade and the specimens filed to the proper size.

### Experimental Procedure for Locating the Ar″

The microscopic technique employed for evaluating the Ar″ in this work is the one described by Greninger and Troiano in their original work on the kinetics of the martensite transformation[3]. In brief, the method consists in quenching a specimen to some temperature within the martensite range, tempering it at an appropriate temperature above the Ar″, and then quenching to room temperature and examining the amount of tempered (black) martensite present. By gradually raising the temperature of the quenching bath, a point is reached at which tempered martensite is no longer present: this temperature is the Ar″, or the so-called M point. This microscopic method, although tedious and time consuming, is very direct, and Greninger (7), in his recent thermal analysis of the Ar″ values of pure iron-carbon alloys and steels, found that the values so obtained are in agreement with the microscopic determinations within ±5 degrees Cent.

The tempering bath temperature used was 300 degrees Cent. (570 degrees Fahr.), except for alloys whose Ar″ points were above

[2]They will be referred to hereafter as slivers.
[3]For a detailed description of the method see reference (2).

275 degrees Cent. (525 degrees Fahr.), in which case a tempering temperature of 320 degrees Cent. (790 degrees Fahr.) was used. In each case, however, preliminary tests were made to ensure that no decomposition to bainite took place during the tempering operation (3-5 seconds).

To keep the variable of austenitizing constant, all specimens of all compositions were austenitized at, and quenched from, the same temperature. Each sliver was held for 20 minutes at 1150 degrees Cent. (2100 degrees Fahr.) to ensure complete solubility of the carbides, then cooled to 900 degrees Cent. (1650 degrees Fahr.), and quenched to the proper temperature. Longer times of solution anneal were found to be unnecessary and to have no effect on the results.

The specimens were suspended on an iron wire and heated in a vertical Pt-Rh wire resistance tube furnace, the temperature of which was automatically controlled. A continuous flow of nitrogen gas, purified over a heated copper wire gauze and dried with anhydrone, was passed through the furnace upwards during heating. Owing to the relatively high austenitizing temperature, however, slight decarburization was often encountered, as evidenced by the premature appearance of martensite at the edges of the samples. To eliminate this, a perforated graphite crucible containing some cast iron chips was suspended in the furnace about 2 inches below the sliver. The nitrogen gas, entering at the bottom of the vertical tube, had to pass through the crucible before striking the sliver, and any remnants of oxygen were thereby eliminated.

For quenching baths, the quaternary eutectic of bismuth, cadmium, lead and tin was used for temperatures up to 300 degrees Cent. (570 degrees Fahr.); for higher quenching temperatures, up to 600 degrees Cent. (1110 degrees Fahr.), pure tin covered with a layer of fine graphite to prevent oxidation was used.

## Results

### *Nickel Series*

In Table I are shown the carbon and nickel contents of the alloys studied. As stated in the discussion of the materials, these alloys may be thought of as plain carbon steels containing nickel in variable quantities as the major alloying element, about 0.20 per cent silicon,

but very little manganese (0.10 per cent, max.), except steel No. 3N which was a commercial S.A.E. 2350 steel and contained 0.60 per cent manganese. The alloy numbers in column 1 correspond to the approximate nickel contents. The results will be described with reference to Figs. 1 to 10.

*Alloy 3N (3.41 per cent nickel)*—At 300 degrees Cent. (570 degrees Fahr.) the first traces of bainite appear after 10 minutes at temperature; after 15 minutes, about 10-15 per cent of the specimen has decomposed (see Figs. 1a and 1b).

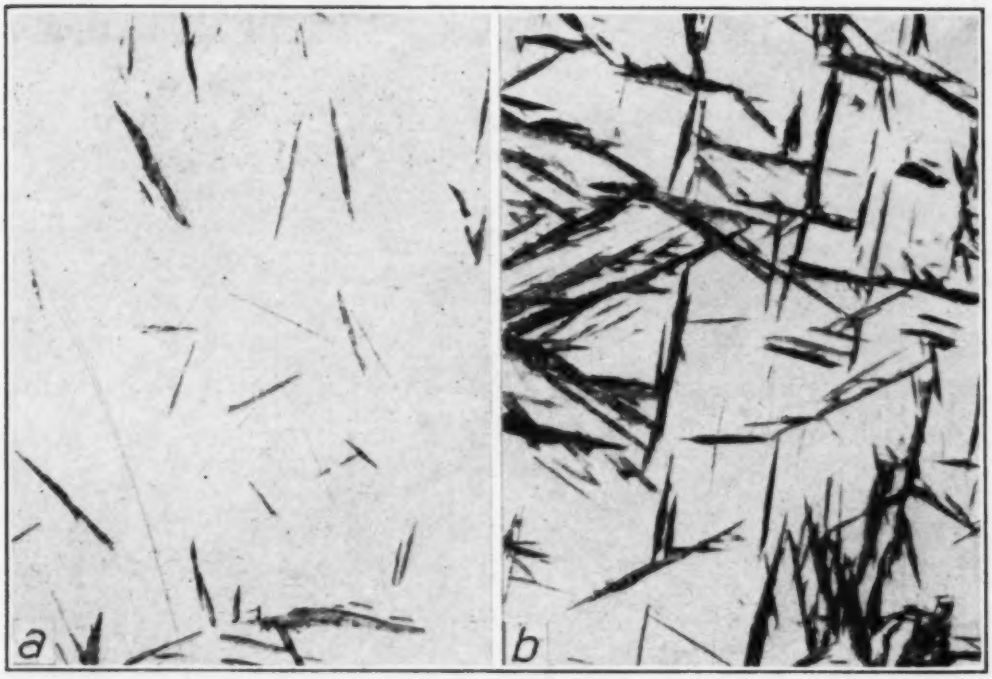


Fig. 1—S.A.E. 2350 Steel (Alloy 3N) Quenched to 300 Degrees Cent. (570 Degrees Fahr.) and Held for Time Intervals Indicated Below. × 500.
(a)—10 Minutes. (b)—15 Minutes.

The first traces of martensite in this alloy were found at 270 ± 5 degrees Cent. (520 degrees Fahr.). Both 1 second and 5 minutes at 265 degrees Cent. (510 degrees Fahr.) result in a characteristic grain boundary envelope of typical martensite needles (see Figs. 2a and 2b); it is only after 15 minutes that bainite begins to form in clusters around the martensite needles already present (see Fig. 2c). The constant temperature decomposition product (bainite) is easily distinguished from the martensite by its tendency to form in clusters and its sharp, needle-like appearance.

Also at 240 degrees Cent. (460 degrees Fahr.) both 1 second

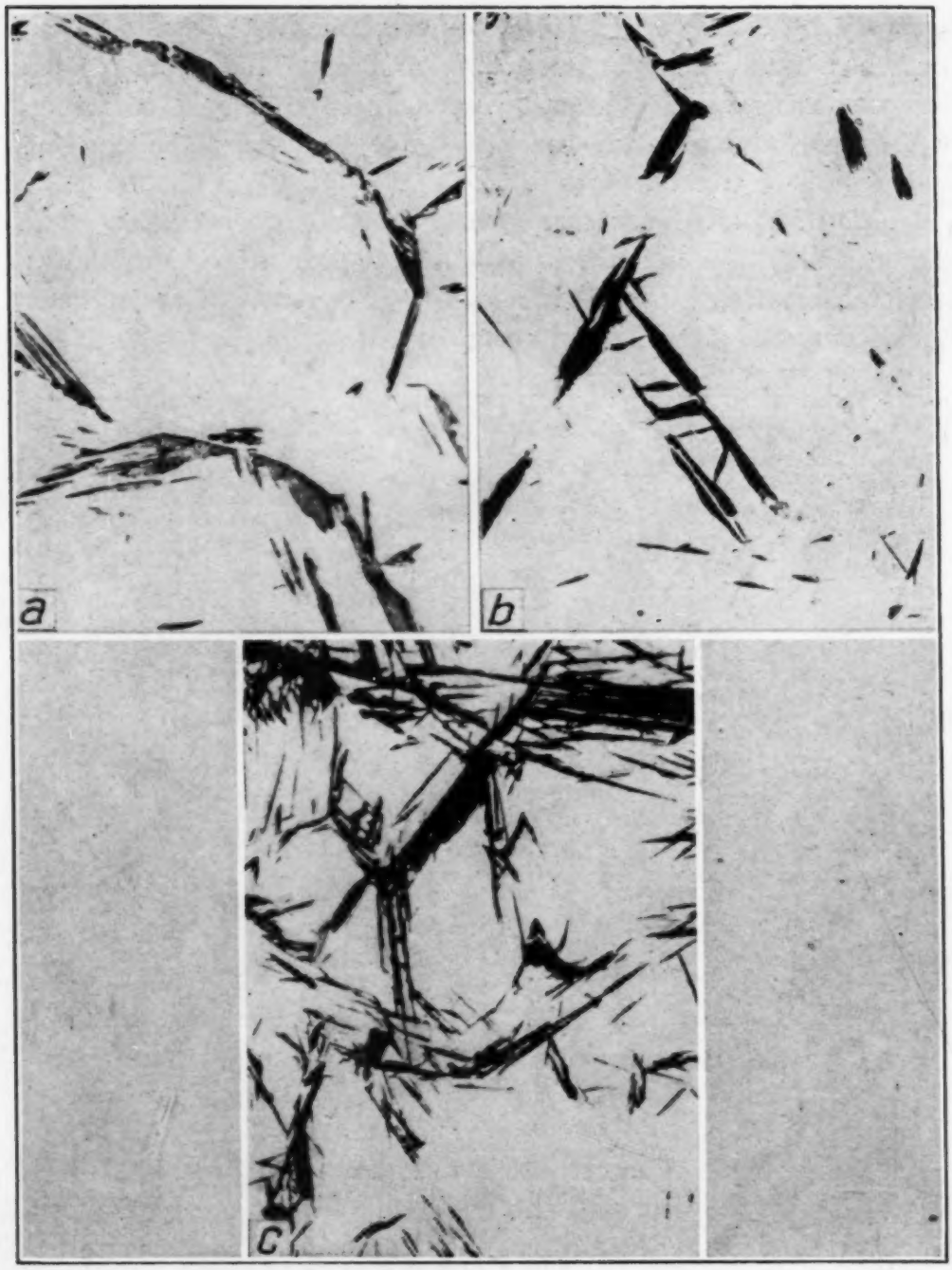


Fig. 2—S.A.E. 2350 Steel (Alloy 3N) Quenched to 265 Degrees Cent. (510 Degrees Fahr.) and Held for Time Intervals as Indicated. × 500.
(a)—1 Second. (b)—5 Minutes. (c)—15 Minutes.

and 5 minutes produced equal amounts of martensite (see Figs. 3a and 3b). It is interesting to note, however, that after 15 minutes at this temperature the amount of bainite is greater than that found in the same time at 265 degrees Cent. (510 degrees Fahr.). This

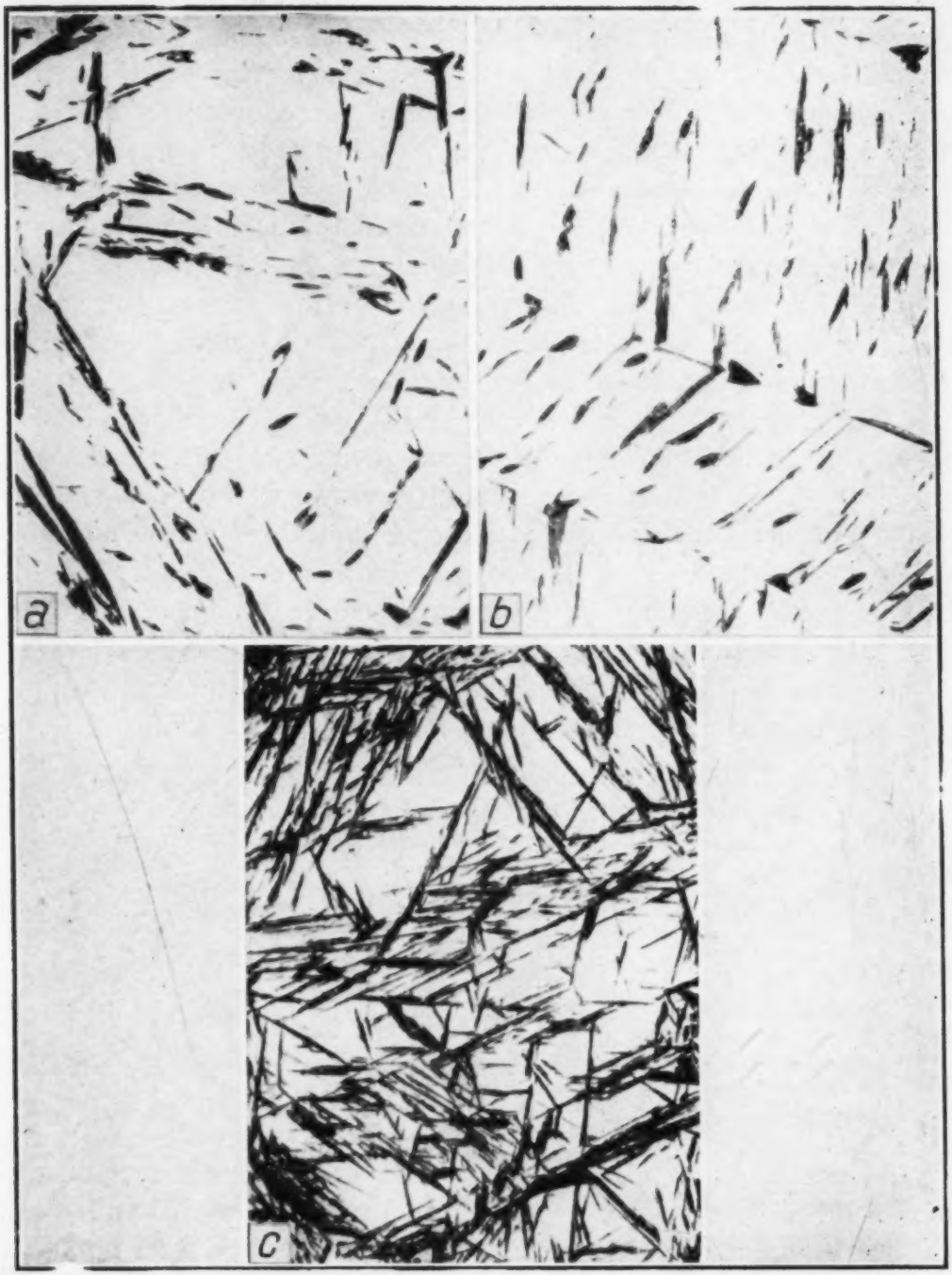


Fig. 3—S.A.E. 2350 Steel (Alloy 3N) Quenched to 240 Degrees Cent. (460 Degrees Fahr.) and Held for Time Intervals as Indicated. × 500.
(a)—1 Second. (b)—5 Minutes. (c)—15 Minutes.

would seem to indicate that the martensite needles nucleate in some way the constant temperature reaction, as evidenced by the fact that the product begins to form and centers about martensite

needles (see Fig. 3c). At 200 degrees Cent. (390 degrees Fahr.), however, no bainite could be found even after 1 hour.

*Alloy 7N (6.62 per cent nickel)*—Increasing the nickel content from about 3 to 7 per cent slows down the bainite reaction considerably, so that at 300 degrees Cent. (570 degrees Fahr.) the first traces of bainite appear after 30 minutes, as compared with 10 minutes in the former alloy. After 45 minutes, the transformation has progressed to cover about 10 per cent of the total volume. The course of transformation in this time interval consists largely of the growth of the small needles already present, rather than in the formation of more needles at new nucleation centers.

The characteristic grain boundary network of martensite begins to develop in this alloy at 230 degrees Cent. (445 degrees Fahr.) (see Fig. 4a). Both 1 second and 10 minutes at this temperature yield equivalent amounts of martensite, indicating that nickel has no effect on the kinetics of the martensite reaction described by Greninger and Troiano for plain carbon steels (compare Figs. 4a and 4b). The first traces of bainite appear at this temperature after 45 minutes, in the form of a fine, hair-like constituent forming preferentially around the martensite needles (Fig. 4c).

**Table I**
**Chemical Analyses* of the Nickel Series Steels**

| Alloy No. | Per Cent Carbon | Per Cent Nickel | Per Cent Manganese |
|---|---|---|---|
| 3N | 0.47 | 3.41 | 0.60 |
| 7N | 0.51 | 6.62 | 0.05 |
| 10N | 0.43 | 10.11 | .... |
| 13N | 0.42 | 13.58 | 0.07 |
| 15N | 0.36 | 14.7 | 0.015 |
| 20N | 0.30 | 21.36 | .... |

*Chemical analysis by W. M. Saunders, official chemist, New England Foundrymen's Association, Providence, R. I.

At 200 degrees Cent. (390 degrees Fahr.), the amount of martensite present is about equal to that found in the 3N alloy at 240 degrees Cent. (465 degrees Fahr.) (compare Fig. 4d with Fig. 3a). This result meets with expectations, as both temperatures are about 35 degrees Cent. below the Ar″ temperatures of the corresponding alloys.

*Alloy 10N (10.11 per cent nickel)*—At 300 degrees Cent. (570 degrees Fahr.) the austenite of this alloy begins to transform to bainite after 2 hours at temperature; the total amount of bainite

Fig. 4—Alloy 7N Quenched to 230 Degrees Cent. (445 Degrees Fahr.) and Held for Time Intervals as Indicated. × 500.
(a)—1 Second. (b)—10 Minutes. (c)—45 Minutes. (d)—1 Second at 200 Degrees Cent.

after 4 hours, however, is not much greater. This seems to indicate an extraordinarily long so-called "incubation period". After an initial formation of nucleation centers, the transformation in the time in-

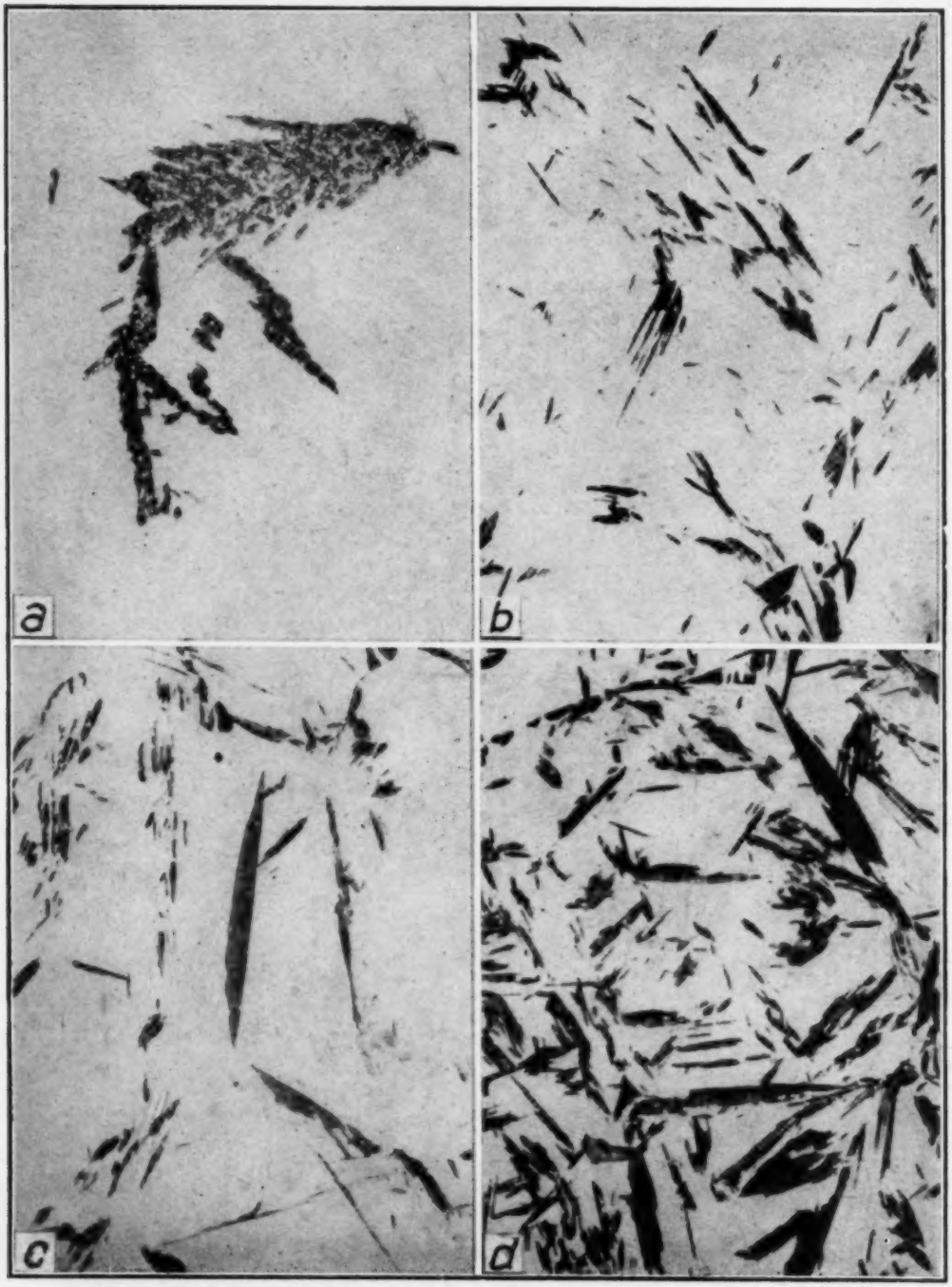


Fig. 5—Alloy 10N Quenched to Various Temperatures and Held for Intervals of Time as Indicated Below. × 500.
(a)—4 Hours at 300 Degrees Cent. (b)—1 Second at 195 Degrees Cent. (c)—2 Hours at 195 Degrees Cent. (d)—1 Second at 160 Degrees Cent.

terval between 2 and 4 hours consists in growth proceeding from these centers. The product is less sharply defined and has a feathery appearance (Fig. 5a).

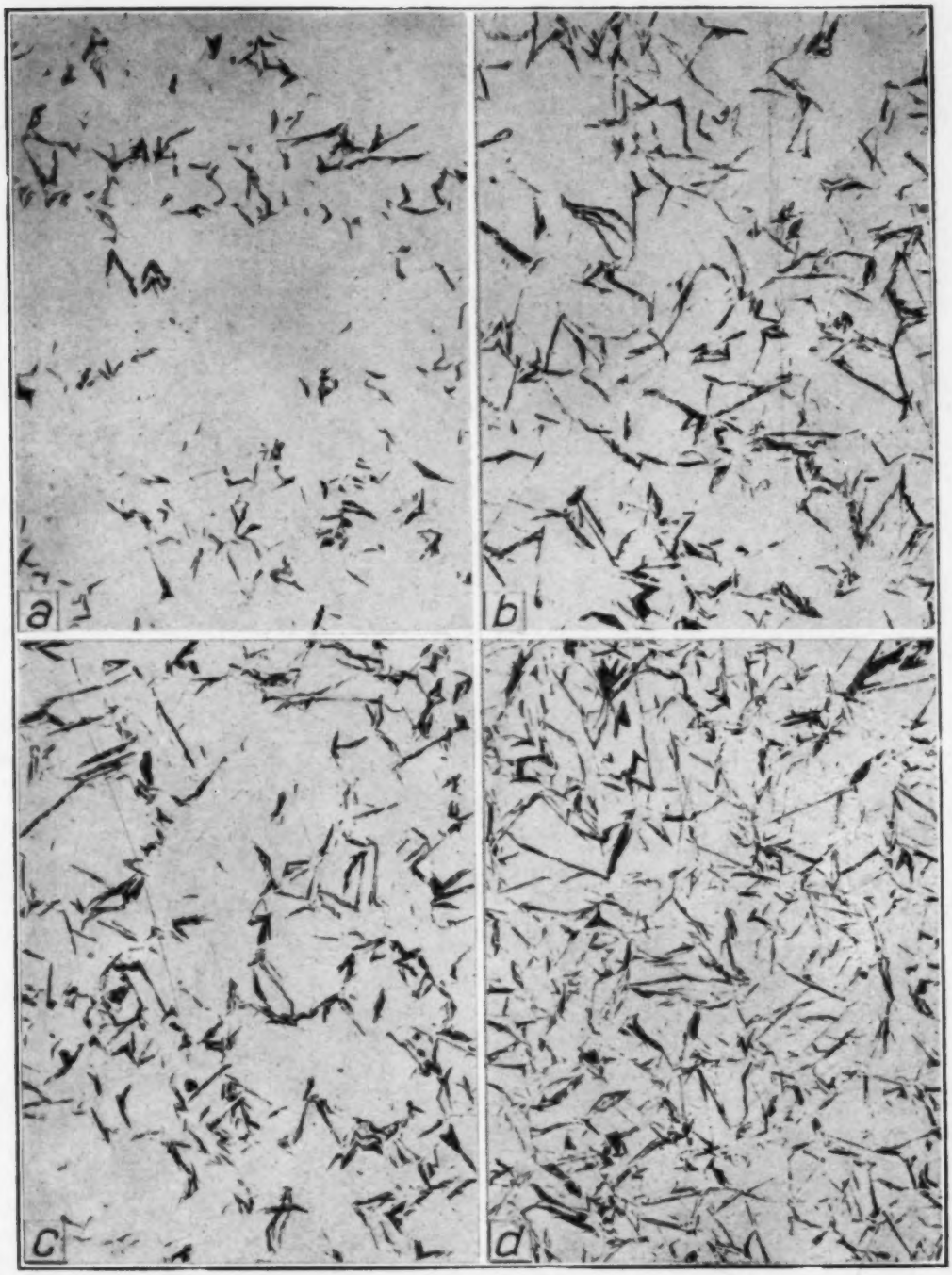


Fig. 6—Alloy 13N Quenched to Various Temperatures and Held for Intervals of Time as Indicated Below. × 150.
(a)—1 Second at 135 Degrees Cent. (b)—1 Second at 115 Degrees Cent. (c)—1 Hour at 115 Degrees Cent. (d)—1 Second at 100 Degrees Cent.

The Ar″ temperature for this alloy was found at 195 ± 5 degrees Cent. (385 degrees Fahr.) as shown in Fig. 5b, the latter representing the amount of martensite present after 1 second

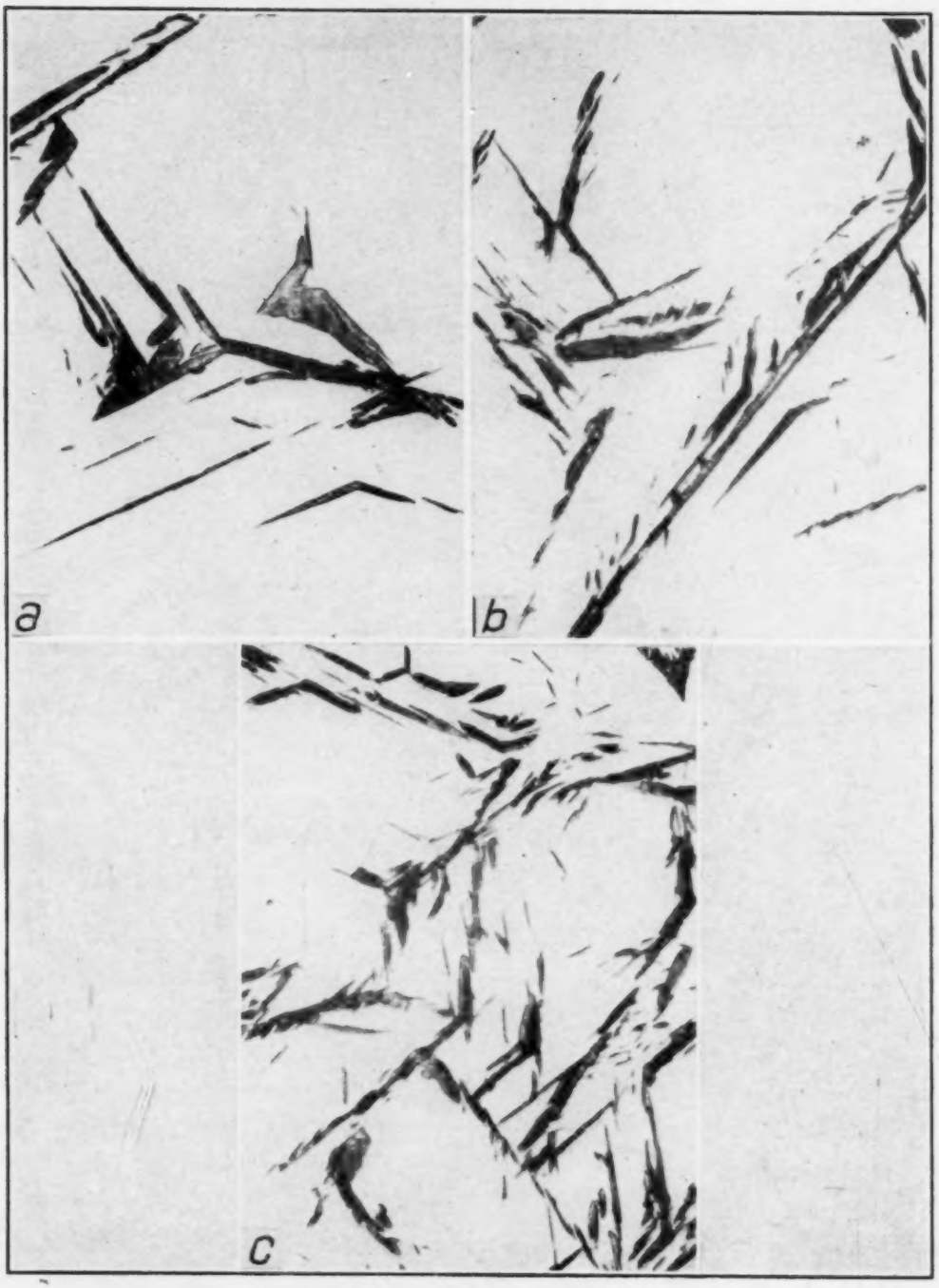


Fig. 7—Alloy 15N Quenched to Various Temperatures and Held for Intervals of Time as Indicated Below. × 500.
(a)—1 Second at 130 Degrees Cent. (b)—1 Second at 120 Degrees Cent. (c)—10 Minutes at 120 Degrees Cent.

at this temperature. Longer times, up to 2 hours, showed no increase in the amount of martensite, and no indications of the presence of bainite (Fig. 5c). The beginnings of martensite formation

are still characterized by a grain boundary network, although less continuous.

At 160 degrees Cent. (320 degrees Fahr.), which is 35 degrees Cent. below the Ar″, the amount of martensite is comparable to that present in the previous alloys 35 degrees Cent. below their corresponding Ar″ points (Fig. 5d compared with Fig. 4d).

*Alloy 13N (13.58 per cent nickel)*—At 300 degrees Cent. (570 degrees Fahr.), no signs of decomposition to bainite were visible even after 65 hours; no longer periods of time were attempted. The Ar″ point for this alloy was found at 135 ± 5 degrees Cent. (275 degrees Fahr.) (see Fig. 6a).

Fig. 8—Alloy 20N Quenched for 1 Second at 65 Degrees Cent. and Tempered 60 Seconds at 300 Degrees Cent.

That the kinetics of the martensite transformation are the same in this alloy as that observed for the alloys described above is well shown by holding a specimen for 1 second and 1 hour at 115 degrees Cent. (240 degrees Fahr.); both time intervals produced equivalent amounts of martensite, as shown in Figs. 6b and 6c. These photomicrographs are purposely shown at ×150 magnification in order to cover the entire width of the specimen for better comparison.

At 100 degrees Cent. (212 degrees Fahr.), 35 degrees Cent. below the Ar″, the amount of martensite present is equivalent to that formed at the corresponding temperatures in the other alloys (Fig. 6d).

*Alloy 15N (14.7 per cent nickel)*—The first traces of martensite in this alloy were found at 130 degrees Cent. (265 degrees Fahr.) (Fig. 7a). The kinetics of the transformation within the martensite range are the same as for all the other compositions (Figs. 7b and 7c).

*Alloy 20N (21.36 per cent nickel)*—Difficulties were encountered in evaluating the Ar″ temperature of this alloy by the microscopic method, and only an approximate value, that of 25 to 75 degrees Cent. (75 to 165 degrees Fahr.) was obtained. The presence of a large volume of austenite seems to affect the relative etching characteristics of white and tempered martensite, so that the distinction between them becomes difficult. One peculiarity noticed was the comparatively long etching time (60 seconds) required to darken the tempered martensite, even though the tempering operation was extended for a period of 60 seconds at 300 degrees Cent. (570 degrees Fahr.).

The microscopic appearance of the martensite in this alloy is considerably different from that in all the previous alloys. The beginnings of martensite formation are no longer characterized by a grain-boundary network, and the needles are generally larger (Fig. 8).

## Discussion of Results

The presence of nickel in austenite considerably retards its subcritical isothermal transformation to bainite, both immediately above the Ar″ point and within the martensite range, thereby permitting a more critical evaluation of the effect of the time variable on the martensite reaction than is usually possible in plain carbon steels. Thus, by way of illustration, a specimen of Alloy 10N, containing 10.1 per cent nickel, could be held at 10 to 15 degrees Cent. within the martensite range for as long as 2 hours without bainite beginning to form. The fact that equal amounts of martensite are present after such widely separated time intervals as 1 second and 2 hours at a given temperature proves conclusively that for all practical purposes the martensite transformation is independent of time. It was further shown, as illustrated in the attached photomicrographs, that specimens of the various nickel steels quenched to a temperature 35 degrees Cent. below their respective Ar″ points contained equivalent amounts of martensite. This in-

dicates that the amount of martensite present in a specimen quenched to a certain temperature within the martensite range is a function of the temperature interval between its Ar″ point and the temperature to which it was quenched, regardless of the absolute value of its Ar″ temperature.

The experimentally determined Ar″ temperatures of the various alloys are shown in Table II, along with the values determined by Greninger (7) for pure iron carbon alloys of equivalent carbon

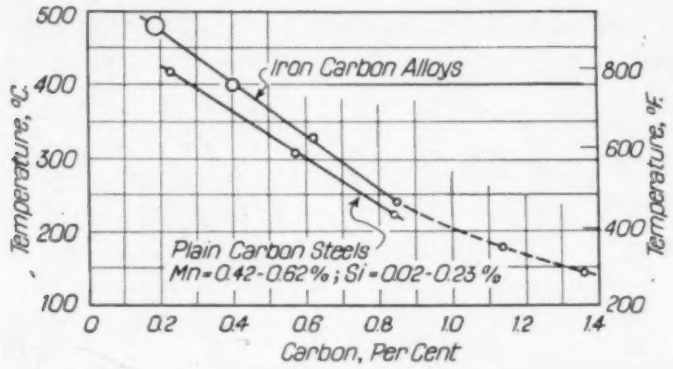


Fig. 9—Influence of Carbon on the Ar″ Temperature of Pure Iron-Carbon Alloys and Plain Carbon Steels. Greninger (7).

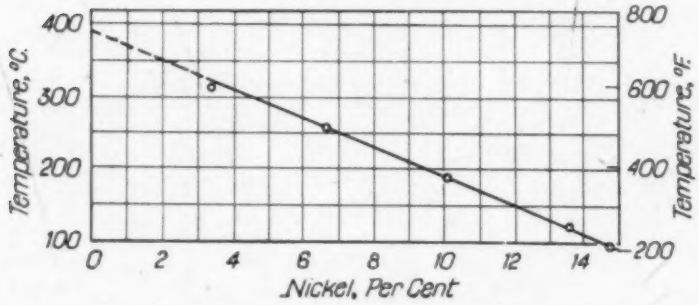


Fig. 10—Influence of Nickel on the Ar″ Temperature of a 0.45 Per Cent Carbon Steel.

contents. In order to be able to plot graphically the influence of nickel on the Ar″ temperatures, the values were adjusted to a common carbon content of 0.45 per cent, as shown in the last column of Table II. The adjustments were made on the basis of the values determined by Greninger (7) for pure iron carbon alloys (see Fig. 9) by simply adding or subtracting the effect of carbon (3.5 degrees Cent. per 0.01 per cent carbon), depending on whether the carbon content of the alloy was above or below 0.45 per cent. In addition, the value for alloy 3N was revised 40 degrees Cent. upwards to

**Table II**
**Ar″ Temperatures of the Nickel Series Steels**

| Alloy No. | Ar″ Temperature in degrees Cent.[3] | Ar″ Temperatures of pure iron-carbon alloys of equivalent carbon contents[1] | Ar″ Temperatures of the nickel steels corrected to 0.45 per cent carbon |
|---|---|---|---|
| 3N | 270 | 375 | 317[2] |
| 7N | 235 | 360 | 257 |
| 10N | 195 | 389 | 188 |
| 13N | 135 | 393 | 124 |
| 15N | 130 | 414 | 97 |

[1]See Fig. 9.
[2]Revised 40 degrees Cent. upwards to account for its 0.60 per cent manganese content. See Fig. 9.
[3]All values are accurate within ±5 degrees Cent.

account for its 0.60 per cent manganese content.[4] The adjusted values fall on a straight line (Fig. 10), which, on extrapolation to 0 per cent nickel, yields a value of 387 degrees Cent. (725 degrees Fahr.) for the Ar″ temperature of a 0.45 per cent carbon steel. This value is in good agreement with that found by Greninger for a 0.45 per cent carbon pure iron-carbon alloy (382 degrees Cent.), in spite of the fact that the steels under discussion contained about 0.20 per cent silicon; however, as will be shown below, silicon has no effect on the Ar″ point. It is concluded, therefore, that nickel

**Table III**
**Chemical Analysis of Molybdenum Series**

| Alloy | Per Cent Carbon | Per Cent Molybdenum | Per Cent Manganese |
|---|---|---|---|
| 1M | 0.48 | 1.45 | 0.08 |
| 2M | 0.74 | 0.97 | .... |
| 3M | 0.81 | 2.23 | .... |
| 4M | 0.86 | 2.08 | 0.05 |
| 5M | 1.01 | 2.09 | 0.09 |

up to 15 per cent lowers the Ar″ temperature of a 0.45 per cent carbon steel uniformly at a rate of about 19 degrees Cent. per 1 per cent nickel.

## Molybdenum Series

The chemical analyses of the molybdenum steels studied are shown in Table III. It will be noted that a carbon content range from 0.52 to 1.01 per cent was covered, the maximum molybdenum content added being about 2 per cent.

[4]As shown in Fig. 9, 0.42-0.62 per cent manganese lowers the Ar″ temperatures of hypoeutectoid pure iron-carbon alloys 40 degrees Cent.

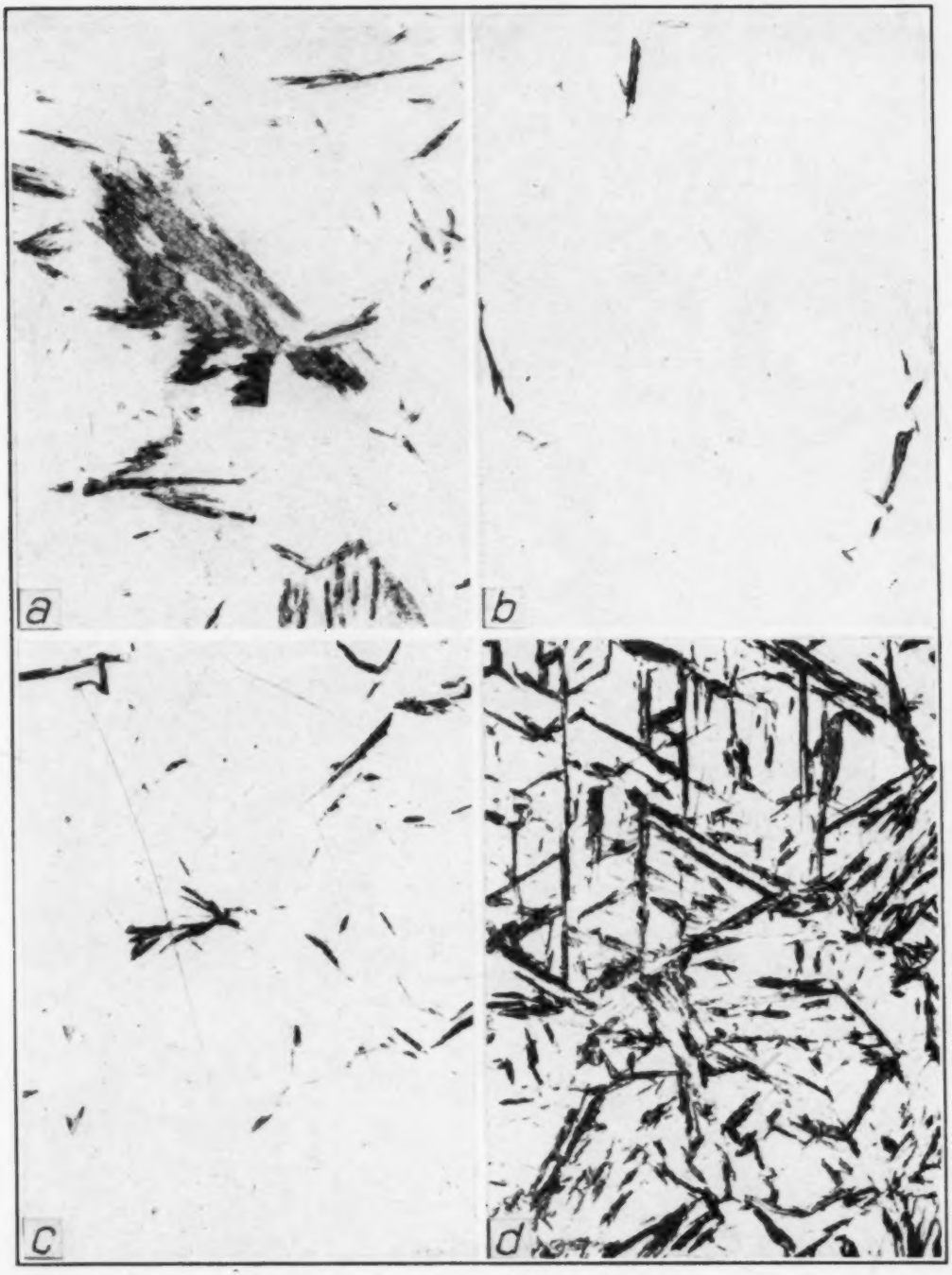


Fig. 11.—Alloy 1M Quenched to Various Temperatures and Held for Intervals of Time as Indicated. × 500.
(a)—10 Seconds at 400 Degrees Cent. (b)—1 Second at 370 Degrees Cent. (c)—1 Second at 350 Degrees Cent. (d)—1 Second at 325 Degrees Cent.

The base alloy for making up composition 1M was the S.A.E. 1050 steel; for compositions 2M, 3M and 4M, the S.A.E. 1085 steel was used; alloy 5M was made from the 1.08 per cent carbon steel.

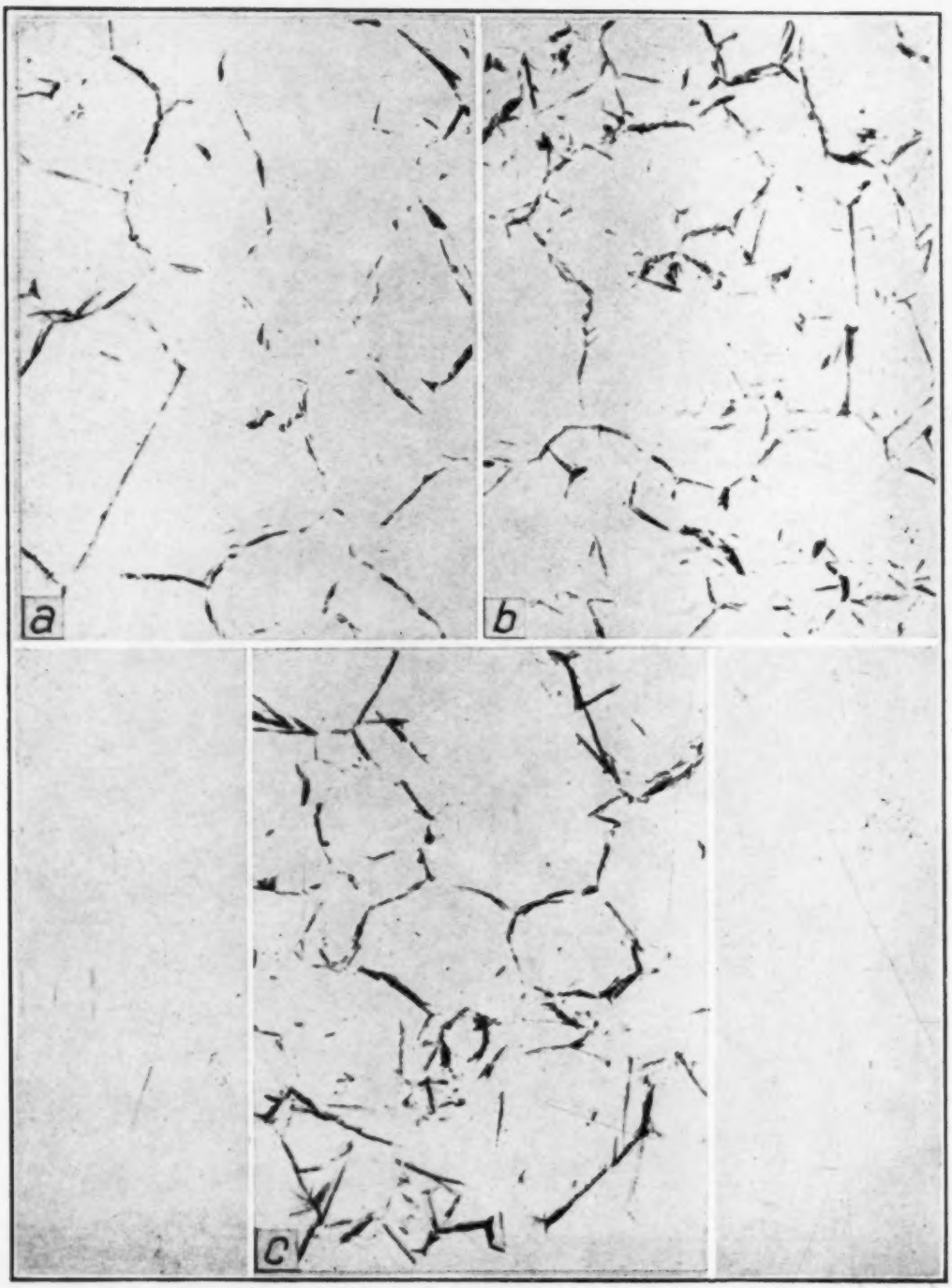


Fig. 12—Alloys 2M, 3M, and 4M Quenched to Various Temperatures and Held for Intervals of Time as Indicated. × 100.
(a)—Alloy 2M, 1 Second at 255 Degrees Cent. (b)—Alloy 3M, 1 Second at 240 Degrees Cent. (c)—Alloy 4M, 1 Second at 225 Degrees Cent.

*Alloy 1M (1.45 per cent molybdenum)* — Owing to the relatively high decomposition rate of this alloy immediately above the

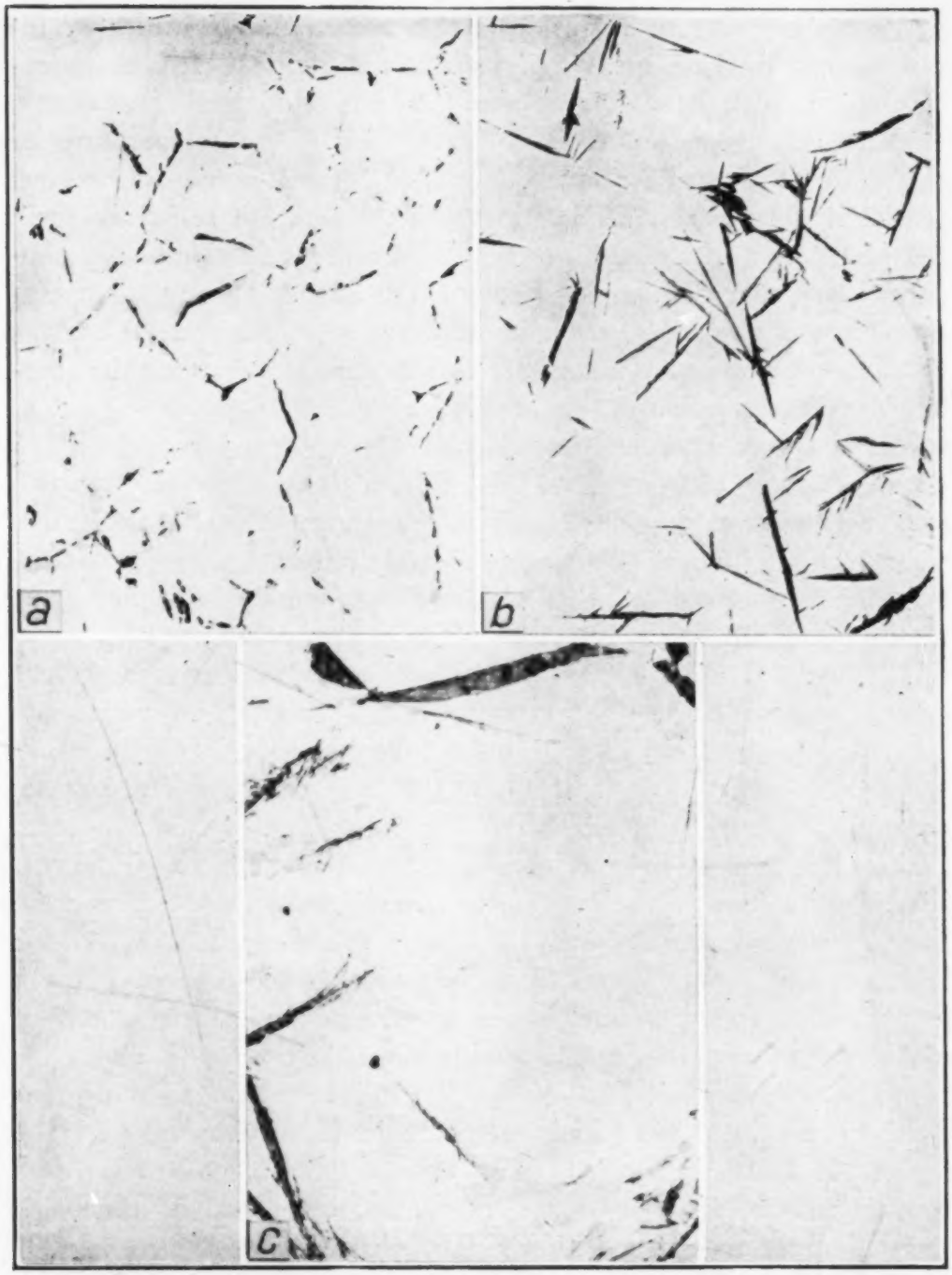


Fig. 13—Alloy 3M Quenched to Various Temperatures and Held for Intervals of Time as Indicated. × 500 Except As Noted.
(a)—1 Minute at 240 Degrees Cent. × 100. (b)—2 Minutes at 300 Degrees Cent. (c)—2 Minutes at 240 Degrees Cent.

Ar″ temperature, where the tempering of the martensite had to be performed, considerable difficulty was encountered in locating the Ar″. The carbon content of this alloy represents about the minimum

necessary in order to be able to locate the Ar″ temperature by the microscopic method, unless, of course, the alloying element appreciably retards the transformation rate at the tempering temperature. Furthermore, because of the relatively high Ar″ temperature of this alloy (375 ± 10 degrees Cent., see below), some of the martensite that forms on cooling to room temperature self-tempers in the process, and may easily be confused with the intentionally tempered dark martensite. In view of the above, the Ar″ temperature for this alloy is reported as accurate only within ±10 degrees Cent., and no attempt was made to study the kinetics of the martensite transformation in this alloy.

The first martensite needles generally appeared at 370 to 375 degrees Cent. (700 degrees Fahr.), although in many samples isolated needles could be found even at 385 degrees Cent. (725 degrees Fahr.) (Figs. 11a and 11b). As the temperature is lowered, the distinction between tempered (dark) and non-tempered (white) martensite becomes more pronounced (Figs. 11c and 11d).

*Alloys 2M, 3M and 4M (0.97, 2.23 and 2.08 per cent molybdenum respectively)* — The characteristic beginnings of martensite formation in the form of a grain-boundary envelope were found at about 265 degrees Cent. (510 degrees Fahr.) for alloy 2M, 250 degrees Cent. (480 degrees Fahr.) for alloy 3M, and 235 degrees Cent. (455 degrees Fahr.) for alloy 4M (Figs. 12a, 12b and 12c). That the kinetics of the martensite transformation are not affected by molybdenum was shown by holding a specimen of alloy 3M for 1 second and 1 minute at 240 degrees Cent. (480 degrees Fahr.); in both time intervals equal amounts of tempered martensite were obtained. (Compare Fig. 13a with Fig. 12b)

The first traces of bainite at 300 degrees Cent. (570 degrees Fahr.) in alloy 3M were found after 2 minutes at temperature (Fig. 13b). At 240 degrees Cent. (480 degrees Fahr.), which is at or a few degrees below the Ar″ point, the same interval of time also showed traces of bainite clustering about the few martensite needles present (Fig. 13c). This is interesting, since one would expect a considerable decrease in the rate of transformation of austenite to bainite on a drop of 50 degrees Cent., especially immediately above the martensite point, and it would seem to indicate that the martensite present serves as nucleation centers for the decomposition to bainite.

*Alloy 5M (2.09 per cent molybdenum)* — The first traces of

**Table IV**
**Ar″ Temperatures of Steels of Molybdenum Series**

| Alloy No. | Ar″ temperatures in degrees Cent.[1] | Ar″ temperatures of pure iron-carbon alloys of equivalent carbon content[2] |
|---|---|---|
| 1M | 375–385 | 371 |
| 2M | 265 | 277 |
| 3M | 250 | 255 |
| 4M | 235 | 233 |
| 5M | 200 | 205 |

[1]Values accurate ±5 degrees Cent.
[2]See Fig. 9.

martensite in this alloy were formed at about 200 degrees Cent. (390 degrees Fahr.); 1 second and 5 minutes at 165 degrees Cent. (330 degrees Fahr.) produced equivalent amounts of tempered martensite, indicating that the kinetics of the transformation remain the same also in this alloy. The microstructure of the products is the same as that shown in Figs. 12 and 13 for alloys 2M, 3M and 4M.

## Discussion of Results

The experimentally determined values of the Ar″ temperatures of the various steels of the molybdenum series are shown in Table IV. A direct comparison of these values with those obtained in pure iron-carbon alloys of equivalent carbon contents[5] reveals that molybdenum up to 2 per cent neither raises nor lowers the Ar″ points of 0.50 to 1.00 per cent carbon steels. That the kinetics of the martensite transformation remain unaffected in the presence of molybdenum additions is abundantly illustrated in Figs. 11 to 13.

## Cobalt Series

Preliminary tests of cobalt-bearing steels have shown that, owing to the increased rate of the bainite reaction, the carbon content had to be confined to hypereutectoid compositions, if the micro-

**Table V**
**Chemical Analysis of Cobalt Series**

| Alloy No. | Per Cent Carbon | Per Cent Cobalt | Per Cent Manganese |
|---|---|---|---|
| 3C | 1.12 | 3.39 | 0.10 |
| 4C | 1.11 | 4.51 | .... |
| 5C | 1.12 | 5.13 | .... |
| 8C | 1.06 | 7.57 | 0.09 |

[5]See Fig. 9.

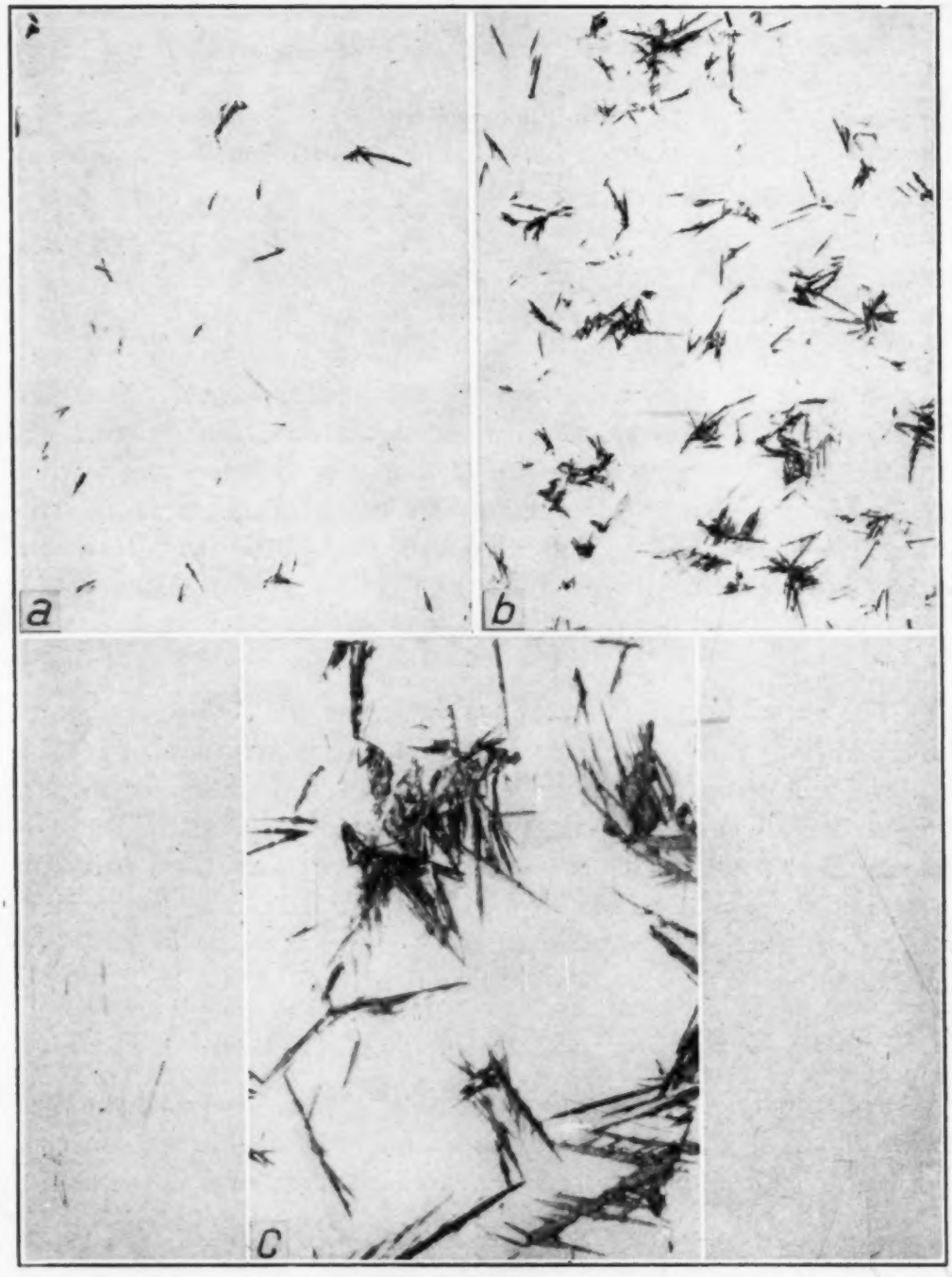


Fig. 14—Alloy 3C Quenched to 300 Degrees Cent. (570 Degrees Fahr.) and Held for Time Intervals as Indicated.
(a)—1.5 Minutes, × 150. (b)—3 Minutes, × 150. (c)—3 Minutes at 300 Degrees Cent. × 500.

scopic method is to be used successfully in determining the Ar″. All the experimental cobalt steels were therefore made up by adding cobalt to a commercial 1.30 to 1.35 per cent carbon drill rod steel.

The chemical analysis of this series of steels is shown in Table V, the numbers of the alloys corresponding to their approximate cobalt contents.

*Alloy 3C (3.39 per cent cobalt)*—The first traces of decomposition to bainite at 300 degrees Cent. (570 degrees Fahr.) were found after 1½ minutes at temperature; after 3 minutes, 5 to 10 per

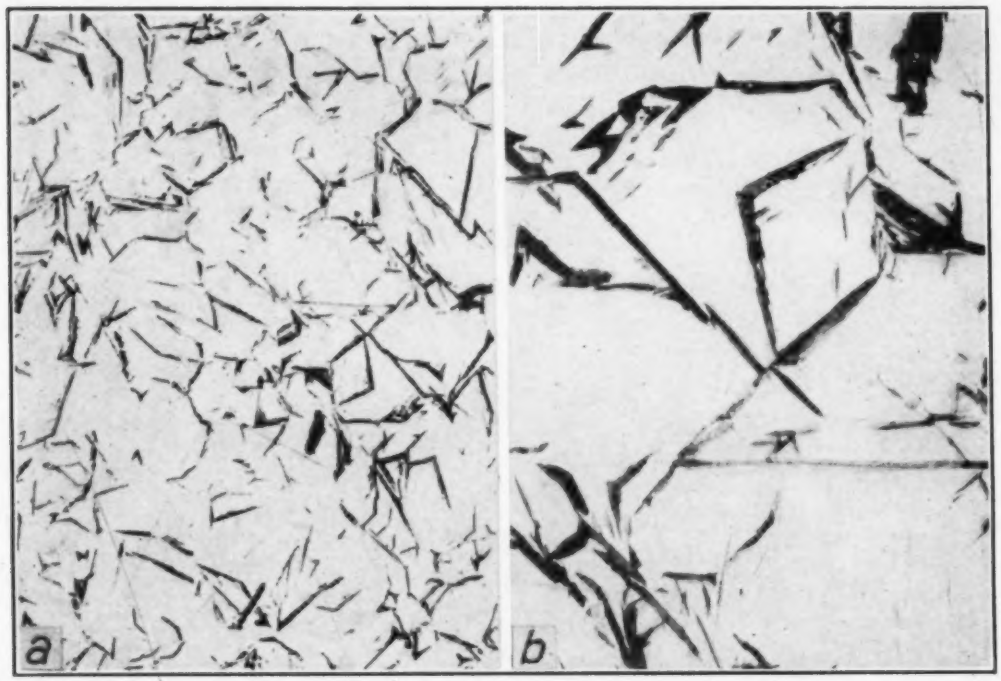


Fig. 15—Alloy 3C Quenched to 190 Degrees Cent. and Held for Time Intervals as Indicated.
(a)—1 Second, × 150. (b)—1 Second, × 500.

cent of the austenite has transformed (Figs. 14a and 14b). The bainite needles characteristically form in clusters, as shown in Fig. 14c.

The amount of tempered martensite present on quenching to 190 degrees Cent. (375 degrees Fahr.) (Figs. 15a and 15b) was equivalent to that usually found at 15 to 20 degrees Cent. below the Ar″ (compare Figs. 15a and 15b with 16d and 17b, the latter representing the amounts of martensite present at 15 to 20 degrees Cent. below the Ar″). The Ar″ temperature for this alloy is, therefore, at 205 ±5 degrees Cent. (400 degrees Fahr.).

*Alloy 4C (4.51 per cent cobalt)*—The beginnings of decomposition to bainite at 300 degrees Cent. (570 degrees Fahr.) were noted after about 40 seconds at temperature, as compared with 1½ minutes for alloy 3C (Fig. 16a). This illustrates well the effect of

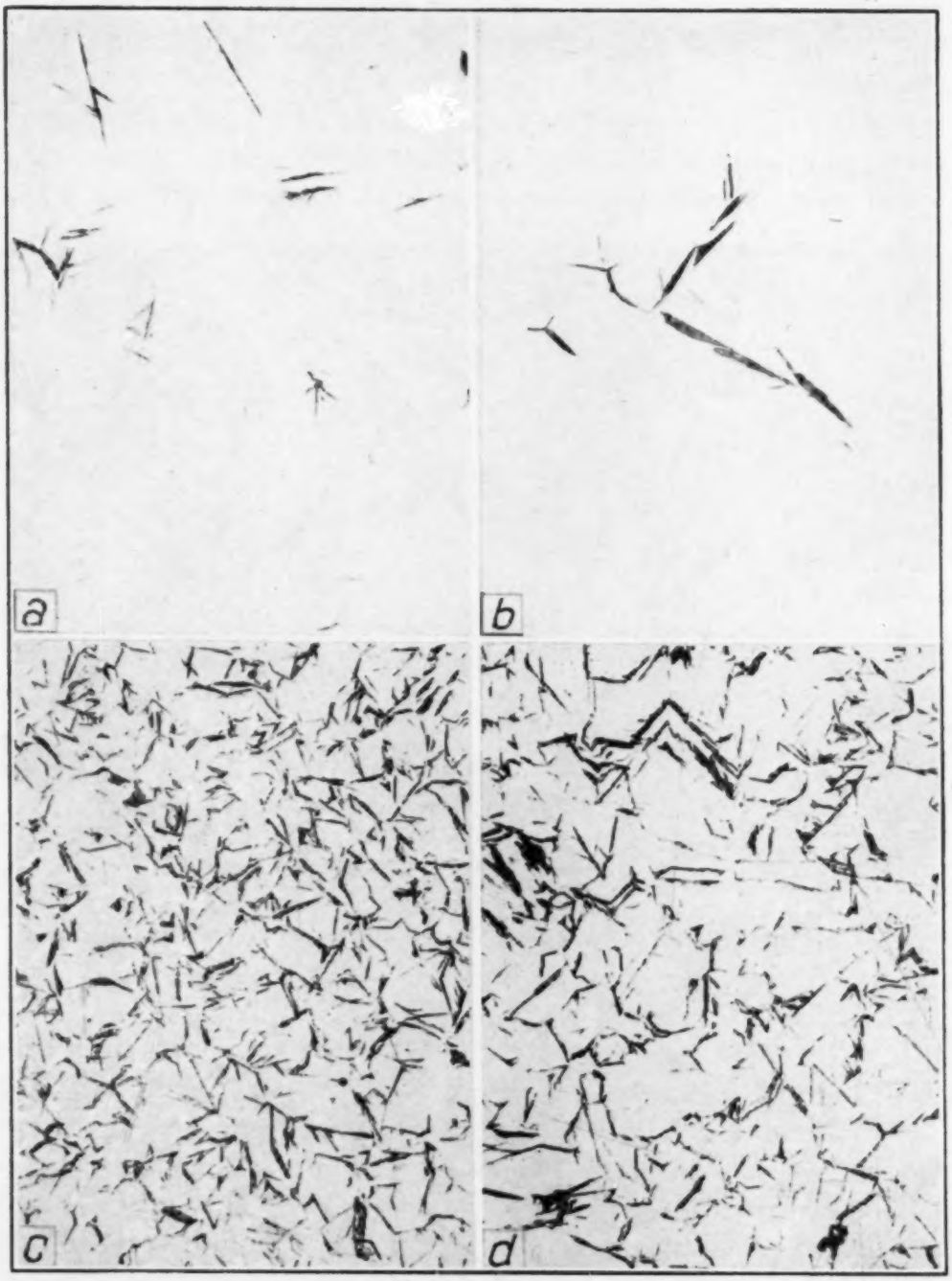


Fig. 16—Alloy 4C Quenched to Various Temperatures and Held for Time Intervals as Indicated. × 500 Except as Noted.
(a)—40 Seconds at 300 Degrees Cent. (b)—1 Second at 225 Degrees Cent. (c)—1 Second at 210 Degrees Cent., × 150. (d)—10 Seconds at 210 Degrees Cent., × 150.

cobalt in increasing the transformation rate of austenite to bainite, and is in agreement with the results reported by Davenport (8).

The very first needles of martensite were found at 225 degrees

Cent. (435 degrees Fahr.) (Fig. 16b). That cobalt does not affect the kinetics of the austenite to martensite transformation was shown by holding one specimen for 1 second and another for 10 seconds at 210 degrees Cent. (410 degrees Fahr.), both yielding equivalent amounts of martensite (Figs. 16c and 16d). A specimen held 1 minute at 210 degrees Cent. (410 degrees Fahr.) showed the presence of small amounts of bainite, in addition to the marten-

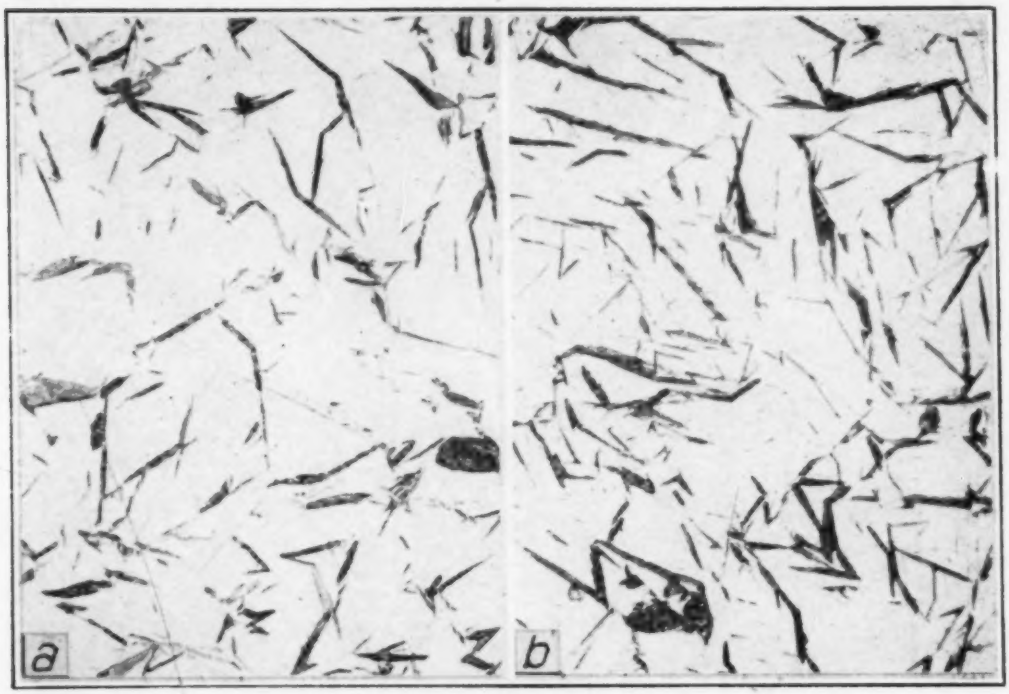


Fig. 17—Alloy 4C Quenched to 210 Degrees Cent. and Held for Intervals of Time as Indicated. × 500.
(a)—1 Second. (b)—1 Minute.

site (compare Figs. 17a and 17b). In view of the fact that at 300 degrees Cent. (570 degrees Fahr.) the very first traces of bainite were found only after 40 seconds, one would hardly expect to find any bainite at all after 1 minute at 210 degrees Cent. (410 degrees Fahr.) unless it is supposed that the presence of small amounts of martensite nucleate the bainite reaction and increase its reaction rate.

*Alloy 5C (5.13 per cent cobalt)*—The amount of bainite present in this alloy after 30 seconds at 300 degrees Cent. (570 degrees Fahr.) is equivalent to that found in alloy 4C after 40 seconds at the same temperature (compare Figs. 18a and 16a.). After 1 minute at 300 degrees Cent. (570 degrees Fahr.), about 50 per cent of the austenite has decomposed (Fig. 18b). When compared with a

Fig. 18—Alloy 5C Quenched to Various Temperatures and Held for Time Intervals as Indicated. × 500.
(a)—30 Seconds at 300 Degrees Cent. (b)—1 Minute at 300 Degrees Cent. (c)—1 Second at 240 Degrees Cent.

plain carbon steel of the same carbon content[6] it appears that 5 per

[6]Davenport (8) reports that a hypereutectoid steel containing 1.13 per cent carbon begins to transform at 300 degrees Cent. (570 degrees Fahr.) after 300 seconds.

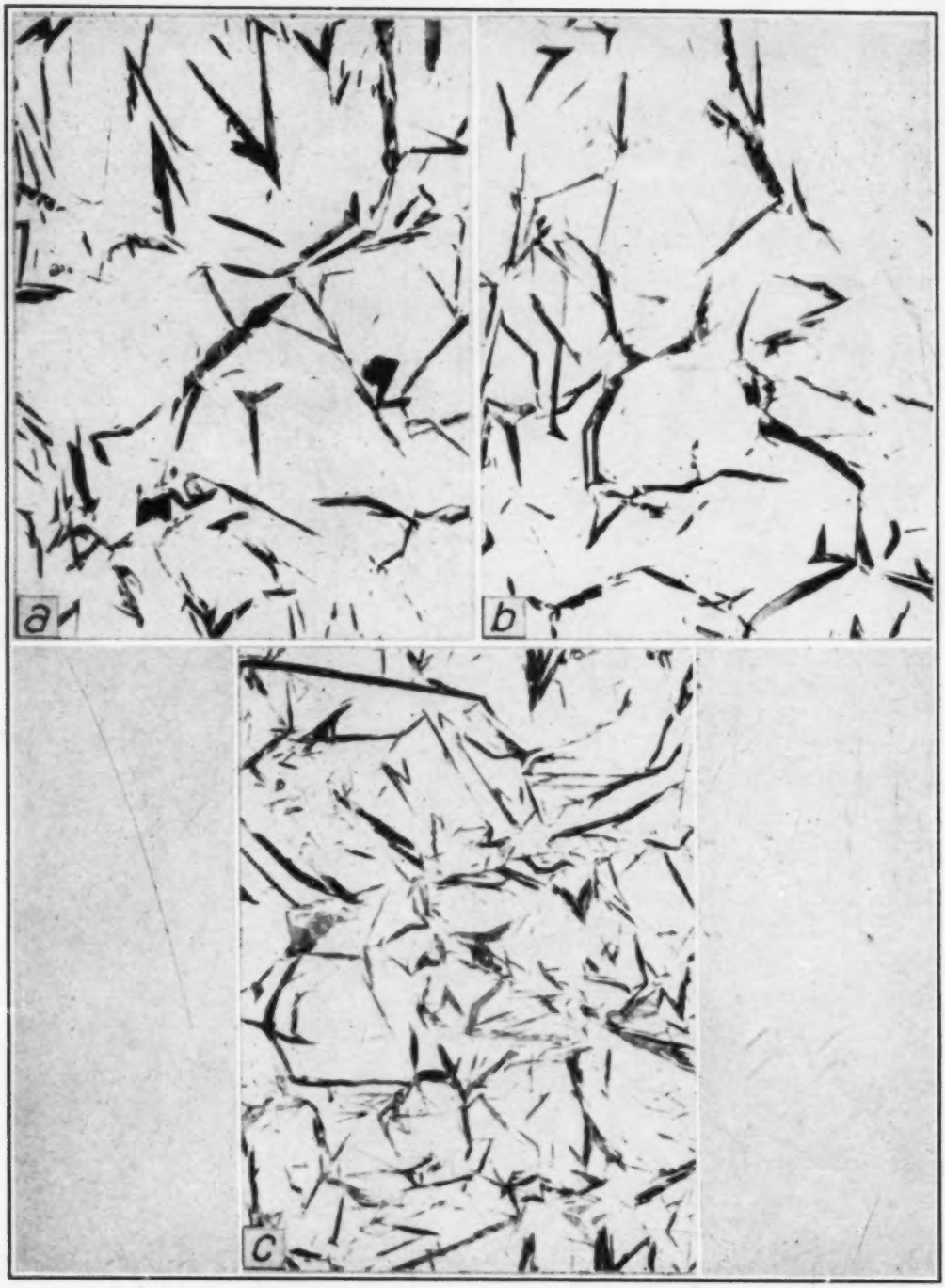


Fig. 19—Alloy 5C Quenched to 225 Degrees Cent. for Time Intervals as Indicated. × 500.
(a)—1 Second. (b)—10 Seconds. (c)—25 Seconds.

cent cobalt increases the decomposition rate of austenite to bainite at 300 degrees Cent. (570 degrees Fahr.) about tenfold.

The first martensite needles in this alloy were found at 240

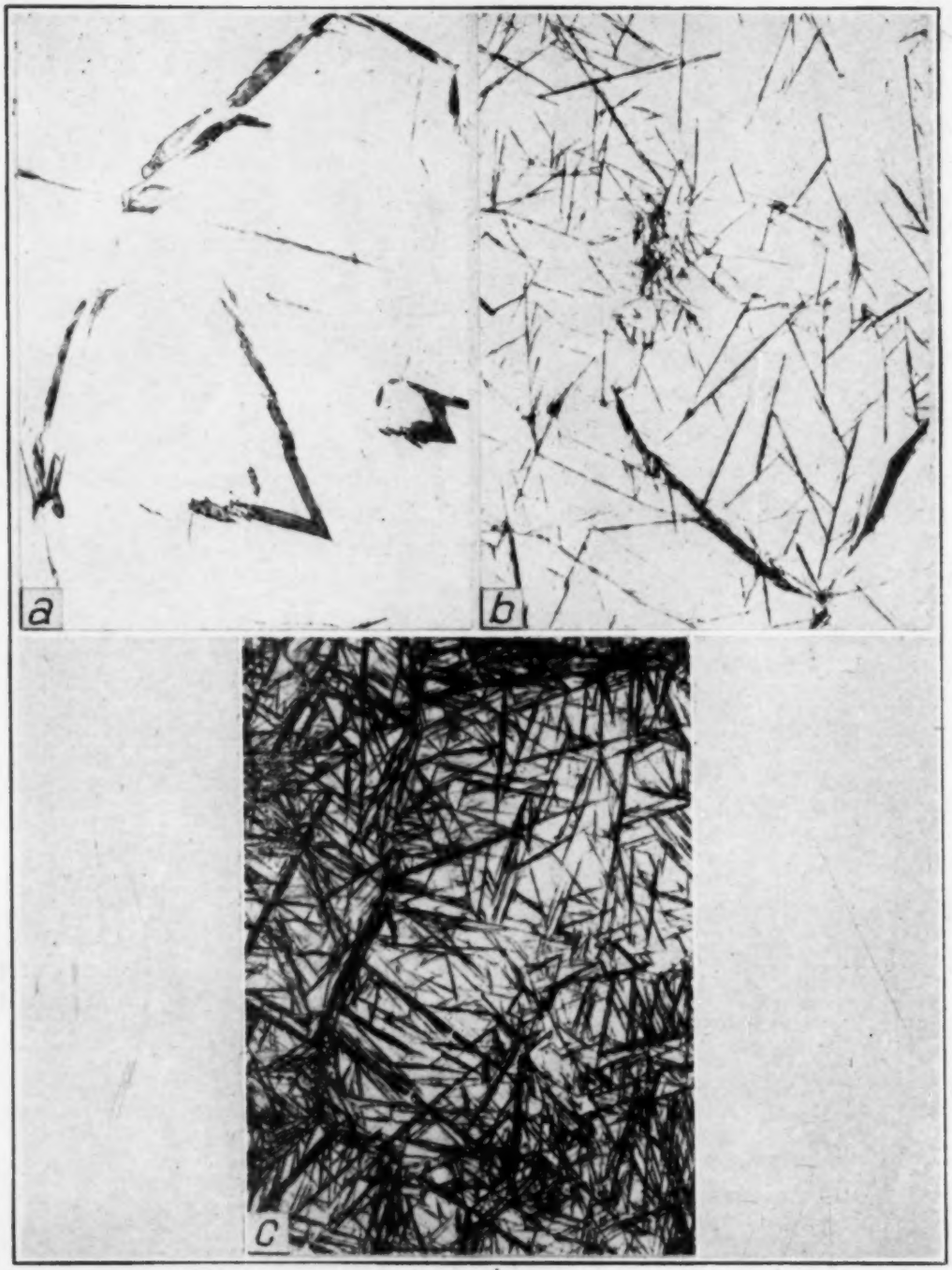


Fig. 20—Alloy 8C Quenched to Various Temperatures and Held for Time Intervals as Indicated. × 500.
(a)—1 Second at 290 Degrees Cent. (b)—5 Seconds at 300 Degrees Cent. (c)—10 Seconds at 300 Degrees Cent.

± 5 degrees Cent. (465 degrees Fahr.) (Fig. 18c). Specimens held for both 1 and 10 seconds at 225 degrees Cent. (435 degrees Fahr.) yielded equal amounts of martensite, indicating that

the kinetics of the martensite transformation remain unchanged (Figs. 19a and 19b). A specimen held 25 seconds at 225 degrees Cent. (435 degrees Fahr.) contained some bainite along with the martensite (Fig. 19c), indicating again that the rate of the bainite reaction at this temperature is greater than or at least equal to the rate at 300 degrees Cent. (570 degrees Fahr.).

*Alloy 8C (7.57 per cent cobalt)*—The Ar″ temperature for this alloy was found at 295 ± 5 degrees Cent. (565 degrees Fahr.) (Fig. 20a). Owing to the relatively high temperature at which the martensite began to form, the temperature of the tempering bath had to be raised. 350 degrees Cent. (660 degrees Fahr.) was found unsuitable, since a specimen held for only 1 second at that temperature showed about 10 per cent bainite. At 320 degrees Cent. (610 degrees Fahr.), however, a specimen held for 1 second showed only isolated needles of bainite; the latter temperature was therefore chosen for the tempering operation. It is for this reason that a specimen held 1 second at 295 degrees Cent. (565 degrees Fahr.) and tempered for 1 second at 320 degrees Cent. (610 degrees Fahr.) contains isolated plates of bainite in addition to the few martensite needles. Fortunately, however, the two types of products are easily distinguished microscopically. (Thin, sharp lines in Fig. 20b are bainite; the thicker, V-shaped structures are martensite.)

At 300 degrees Cent. (570 degrees Fahr.), the rate of decomposition to bainite is indeed very rapid; a specimen held 10 seconds at that temperature was nearly 50 per cent decomposed (Figs. 20b and 20c). When compared with Alloy 5C, which required about 1 minute to affect a 50 per cent decomposition, it appears that an increase in the cobalt content from 5.13 per cent to 7.57 per cent multiplies sixfold the decomposition rate of the bainite reaction.

## Discussion of Results

As has been shown originally by Davenport (8) cobalt is the only alloying element known to increase the subcritical transformation rate of austenite to bainite. This is confirmed qualitatively by the results of the present work. The experimentally determined Ar″ temperatures of the cobalt series steels are shown in Table VI. The influence of increasing cobalt contents on the Ar″ point of a 1.12 per cent carbon steel is shown graphically in Fig. 21. From 3.31 to

7.57 per cent, cobalt raises the Ar″ temperature of a 1.12 per cent carbon steel uniformly at a rate of 19 degrees Cent. per 1 per cent cobalt. So far as is presently known, cobalt is the only alloying element that raises the Ar″ point. The significance of the relationship between its effects in increasing the rate of the bainite reaction and in raising the Ar″ temperature is not clear. When extrapo-

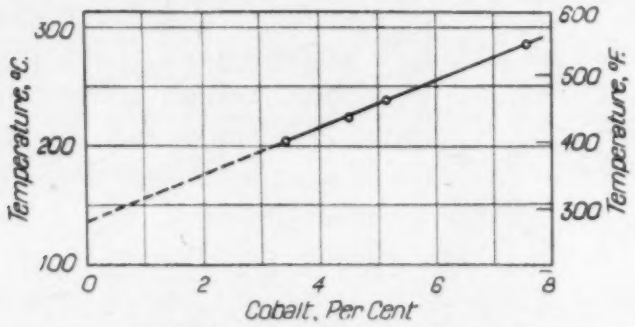


Fig. 21—Influence of Cobalt on the Ar″ Temperature of a 1.12 Per Cent Carbon Steel.

lated to 0 per cent cobalt, the graph of Fig. 21 yields a value of 240 degrees Cent. (465 degrees Fahr.) for the Ar″ temperature of a 1.12 per cent carbon steel. This value is 43 degrees Cent. below that reported by Greninger (7) for a 1.12 per cent carbon pure iron-carbon alloy (see Fig. 9). The cause for this discrepancy is not clear, except that at least part of it may be due to the fact that the cobalt alloys contained about 0.10 per cent manganese. Further-

Table VI
Ar″ Temperatures of Steels of the Cobalt Series

| Alloy No. | Ar″ temperatures degrees Cent.[1] | Ar″ temperatures of pure iron-carbon alloys of equivalent carbon contents[2] |
|---|---|---|
| 3C | 205 | 183 |
| 4C | 225 | 182 |
| 5C | 240 | 183 |
| 8C | 295 | 193 |

[1]Values accurate within ±5 degrees Cent.
[2]See Fig. 9.

more, it may also indicate that either at lower cobalt contents the influence is not uniform, or that small additions of cobalt even lower the Ar″ point somewhat.

## Silicon Series

The chemical compositions of the three silicon alloy steels studied are shown in Table VII, along with the Ar″ temperature

found for each alloy. A comparison of these values with those obtained by Greninger for pure iron-carbon alloys of equivalent carbon contents reveals that silicon up to 3.65 per cent (highest composition studied) neither raises nor lowers the Ar″ point of 0.70 to 0.85 per cent plain carbon steels. Similarly, in close agreement with the results obtained in the nickel, cobalt and molybdenum steels,

**Table VII**
**Chemical Composition and Ar″ Temperatures of Steels of the Silicon Series**

| Alloy No. | Per Cent Carbon | Per Cent Silicon | Per Cent Manganese | Ar″ temperature[1] | Ar″ temperature of pure iron-carbon alloys of equivalent carbon contents[2] |
|---|---|---|---|---|---|
| 1S | 0.72 | 1.62 | 0.08 | 275 | 284 |
| 2S | 0.83 | 2.53 | 0.10 | 240 | 244 |
| 3S | 0.84 | 3.65 | 0.07 | 240 | 240 |

[1]Values accurate ±5 degrees Cent.
[2]See Fig. 9.

silicon was found to affect in no way either the kinetics or the mechanism of the austenite to martensite transformation. No photomicrographs are attached in support of these results, as they are identical in appearance with those of the other alloy steels having equivalent Ar″ temperatures.

## Conclusions

Nickel, molybdenum, cobalt and silicon have been shown individually to alter in no way either the kinetics or the mechanism of the austenite to martensite transformation in steels described by Greninger and Troiano for plain carbon steels, while the bainite reaction is retarded by nickel, molybdenum or silicon, and speeded up by cobalt; the instantaneous nature of the martensite transformation remains unaffected by these alloying elements. As in the case of plain carbon steels, it was shown that also in these alloy steels the amount of martensite present in a sample quenched to some temperature within the martensite range is a function of the magnitude of the temperature interval between the Ar″ and the quenching bath temperature, and is, for all practical purposes, independent of the length of time held at that temperature.

In a 0.45 per cent carbon steel, nickel, up to 15 per cent, lowers

the Ar″ temperature at a uniform rate of 19 degrees Cent. per 1 per cent nickel.

Molybdenum, up to 2 per cent, neither raises nor lowers the Ar″ points of either 0.50 per cent, 0.80 per cent, or 1.00 per cent carbon steels.

Similarly, silicon up to 3.5 per cent neither raises nor lowers the Ar″ points of 0.72 to 0.84 per cent carbon steels.

Cobalt, from 3.4 to 7.6 per cent, raises the Ar″ point of a 1.12 per cent carbon steel uniformly at a rate of about 19 degrees Cent. per 1 per cent cobalt; this rate, however, may not hold at lower cobalt contents.

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## DISCUSSION

**Written Discussion:** By E. P. Klier, assistant instructor, and A. R. Troiano, associate professor of metallurgy, University of Notre Dame, Notre Dame, Ind.

Several papers presented at this meeting have been devoted almost entirely to a study of the effect of various alloying elements on Ar″ in steel. However, none of these investigators have made any reference to a rather comprehensive

investigation of this nature by Zyuzin, Sadovski and Baranchuk[7]. It is recognized that considerable of the data of Zyuzin et al. may be in error quantitatively, yet due to its qualitative correctness and the number of alloying elements studied, we believe this work should be indicated. In Table A, the results of investigations presented at this meeting plus the results of Zyuzin et al. are presented in order of effectiveness in lowering Ar″. It is seen that manganese,

**Table A**
**Change of Ar″ per 1 Per Cent Alloying Element**

| Element | Zyuzin et al[7] | Payson and Savage[a] | |
|---|---|---|---|
| Mn | —100° F. = —50° C.<br>app. 0.9 to 1.0% C. | —60° F. = —33° C.<br>app. 0.45% C. | —66° F. = —38° C.[10]<br>app. 0.50% C. |
| Cr | —27° F. = —15° C.<br>app. 0.9 to 1.0% C. | —50° F. = —28° C.<br>app. 0.50 to 0.55% C. | —40° F. = —22° C.[b]<br>app. 0.4% C. |
| Ni | —31° F. = —17° C.<br>app. 0.9 to 1.0% C. | —30° F. = —16.5° C.<br>app. 0.46% C. | *—34° F. = —19° C.<br>adjusted to 0.45% C. |
| Cu | —18° F. = — 10° C.<br>app. 0.9 to 1.0% C. | | |
| Mo | variable 0 to —50° C.<br>app. 0.9 to 1.0% C. | —13° F. = —7° C.<br>app. 0.49% C. | * 0<br>0.5, 0.8 and 1.0% C. |
| W | variable 0 to —50° C.<br>app. 0.9 to 1.0% C. | —7° F. = —4° C.<br>app. 0.46 to 0.53% C. | |
| V | variable 0 to —50° C.<br>app. 0.9 to 1.0% C. | — | 0[c]<br>Wide carbon range |
| Si | 0<br>app. 0.9 to 1.0% C. | —20° F. = —11° C.<br>0.47%C., one steel only | * 0<br>app. 0.7 to 0.85% C. |
| Co | 22° F. = 12° C.<br>app. 0.9 to 1.0% C. | | * 34° F. = 19° C.<br>app. 1.1% C. |
| Al | 54° F. = 30° C.<br>0.76% C. | | |

*Chiswik and Greninger.

[a]Payson and C. H. Savage, "Martensite Reactions in Alloy Steels," TRANSACTIONS, American Society for Metals, Vol. 33, 1944, p. 261.

[b]This discussion.

[c]F. Wever and A. Rose, *Mitteilungen aus dem Kaiser Wilhelm Institut für Eisenforschung*, Vol. 20, 1938, p. 213-227.

chromium, nickel and copper may be considered effective in lowering Ar″ while for practical purposes molybdenum, silicon, tungsten and vanadium do not affect Ar″. Copper and aluminum additions definitely elevate Ar″. Certain quantitative discrepancies are noted in the values presented by the various authors. However, these need not be considered serious, since for the most part, they are due to lack of complete data.

In Fig. 22 are given the results of our work on a series of chromium steels containing approximately 0.40 per cent carbon. The method of determining Ar″ was the same as employed in the work under discussion. The observed values of Ar″ have been corrected as indicated. (Carbon to 0.40 per cent, chromium to multiples of 3 per cent.) For very dilute solutions in low carbon steels chromium may actually raise Ar″ as has been indicated by the data of Rose and Fischer.[8] It can be seen from Fig. 22 that a maximum also may exist for 0.40 per cent carbon-chromium steels. (The value for Ar″ for 0.40 per cent carbon steel with 0.20 per cent manganese was obtained from the data of Greninger[9] and is at about 380 degrees Cent. (715 degrees Fahr.). This is

[7]V. Zyuzin, V. Sadovski and S. Baranchuk, *Metallurg*, Vol. 14, Nos. 10-11, 1939, p. 75-80.

[8]A. Rose and W. Fischer, *Mitteilungen aus dem Kaiser Wilhelm Institut für Eisenforschung*, Vol. 21, 1939, p. 133-145.

[9]A. B. Greninger, "The Martensite Thermal Arrest in Iron-Carbon Alloys and Plain Carbon Steels," TRANSACTIONS, American Society for Metals, Vol. 30, 1942, p. 1139-1158.

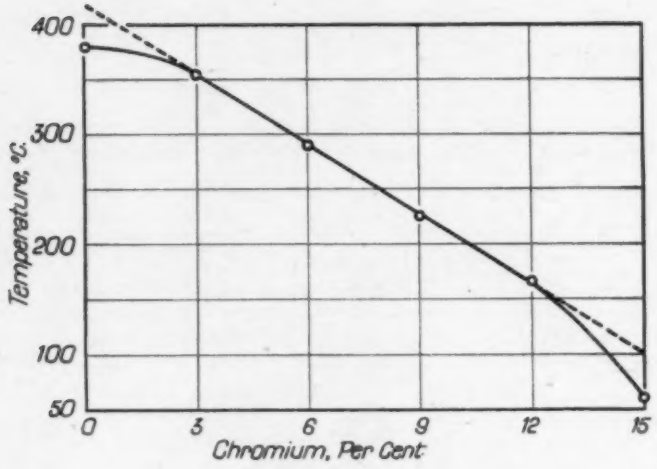


Fig. 22

| Cr | C | Ar″ (obs.) | Ar″ (cor.) |
|---|---|---|---|
| | | ⌐Degrees Cent.¬ | |
| 2.90 | 0.38 | 365 | 355 |
| 5.53 | 0.43 | 290 | 289 |
| 8.77 | 0.41 | 223 | 225 |
| 11.75 | 0.46 | 152 | 167 |
| 14.61 | 0.42 | 65 | 62 |

Manganese content 0.20 to 0.25 per cent.
Extrapolated value Ar″—420 degrees Cent.
Ar″ for 0.20 per cent manganese, 0.40 per cent.
Carbon steel—380 degrees Cent.
Correction factors: 0.01 per cent carbon—3.5 degrees Cent., 1.0 per cent chromium—25 degrees Cent.

approximately 40 degrees Cent. (105 degrees Fahr.) less than the value obtained by extrapolating the straight line portion of our curve to 0 per cent chromium.) It would be veritably impossible to detect the occurrence of such a phenomenon using the method that has been employed here. Between 3 and 12 per cent chromium appears to lower Ar″ at a constant rate. This is no longer true above 12 per cent chromium. Extrapolation yields a value of 100 degrees Cent. (210 degrees Fahr.) for Ar″ in a 15 per cent chromium steel, 35 degrees Cent. (95 degrees Fahr.) above the observed value. This discrepancy may be due to the fact that the effect is real, the method of determination is inadequate, or the austenite is stabilized. Any one or combination of these three factors may be active, for the available experimental data do not allow a positive stand on this matter.

The effect noted for low chromium alloys is probably analogous to the effect observed for the cobalt steels. For the reasons already noted the effect observed for high chromium steels may also be present under analogous circumstances for other steels, notably in the nickel steels presented above and in the manganese steels as indicated by the data of Russell and McGuire.[10]

It has been indicated by the authors in several instances that martensite may nucleate the intermediate reaction. The evidence presented in some instances does indicate this to be true, but considerable other evidence indicates that this definitely is not the case. This proof results from the fact that such

[10]J. V. Russell and F. T. McGuire, "A Metallographic Study of the Decomposition of Austenite in Manganese Steels," TRANSACTIONS, American Society for Metals, Vol. 33, 1944, p. 103.

nucleation demands an increased rate of reaction with increasing martensite content, whereas, actually the reverse is found to be true.[11, 12]

It would be interesting to know if the authors held any specimens at constant

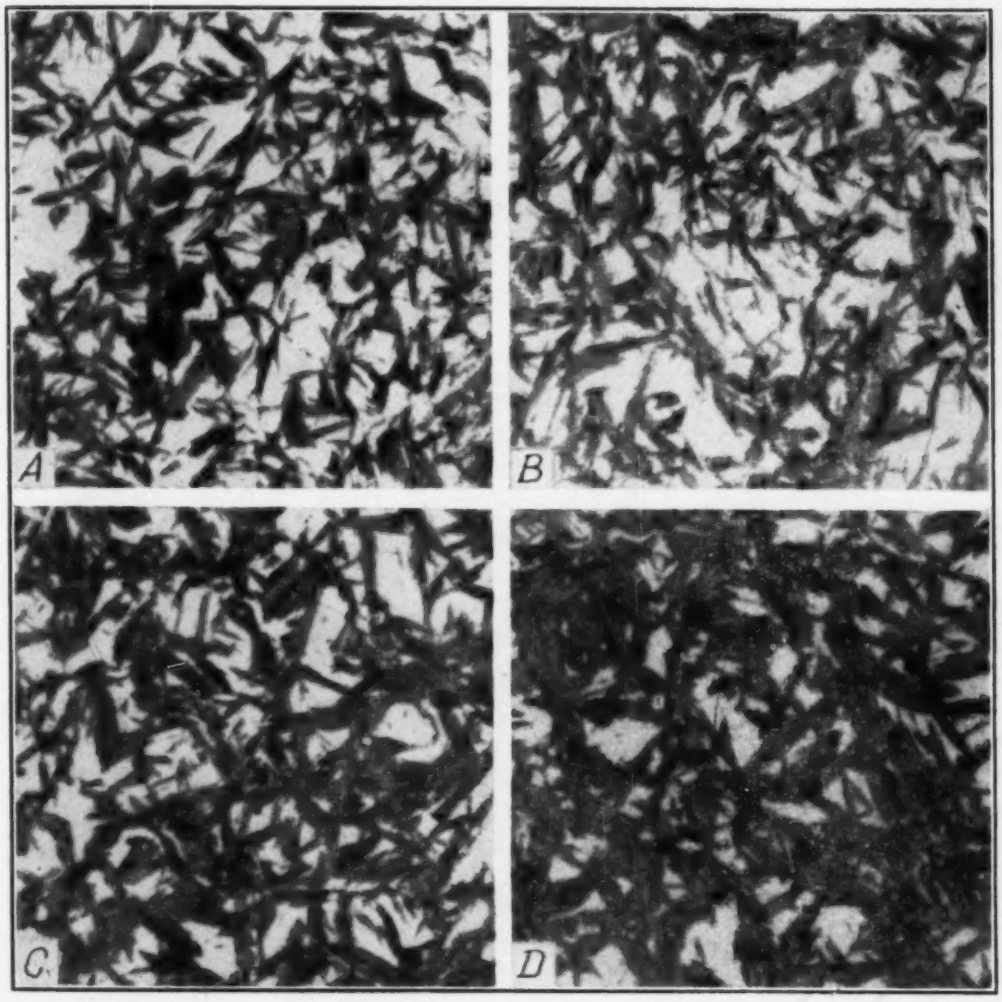


Fig. 23—Effect of Tempering Time on the Martensite Determination. AISI-C1095 Steel—Carbon 0.91 Per Cent, Manganese 0.46 Per Cent. Austenitized 1550 Degrees Fahr., 60 Seconds. Quenched in Oil 300 Degrees Fahr., 15 Seconds. Tempering Temperature, 700 Degrees Fahr. × 750. A—3 Seconds. B—5 Seconds. C—10 Seconds. D—15 Seconds.

temperature for relatively long times and, if so, what the resultant microstructures were.

### Oral Discussion

H. J. ELMENDORF:[13] The authors are to be commended for their excellent paper which has filled in so many voids in the data known concerning the effect of alloying elements on the Ar″ transformation in steel. We are gratified that

[11]E. P. Klier, discussion, TRANSACTIONS, American Society for Metals, Vol. 33, 1944, p. 236.

[12]D. P. Antia, TRANSACTIONS, American Society for Metals. Discussion, "High Chromium Steels," Vol. 31, 1943, p. 408-410.

[13]Research engineer, American Steel & Wire Co., Cleveland.

complete data have been presented on the negligible effect of molybdenum on the Ar″ point which has corroborated our work on a single molybdenum steel.

It is particularly interesting to note that both in this paper and the Payson and Savage paper strict attention has been paid to the selection of the tempering temperature and time for the martensite determination in that the cycles have been so chosen that transformation of the remaining austenite to bainite is precluded. In the martensite determination for plain carbon steel, we have often observed the presence of bainite which is very likely to result in erroneous ratings for the amount of martensite present and accordingly we have always selected suitable cycles. The effect of tempering time at a tempering temperature of 370 degrees Cent. (700 degrees Fahr.) is shown in Fig. 23 for a 0.91 per cent carbon steel wherein it is observed that the austenite to bainite transformation has started in 5 seconds. This is very interesting when it is remembered that the isothermal transformation starting time at 370 degrees Cent. (700 degrees Fahr.) for this steel is approximately 40 seconds. It should be remembered that this steel has been quenched at 150 degrees Cent. (300 degrees Fahr.) and has considerable martensite present which of course accelerates the bainite transformation.

It has been stated that the martensite nucleates the bainite transformation. This is no doubt true as we too have seen that in most cases the bainite transformation starts at the martensite needle interface; however, we do not believe that the nucleation hypothesis explains the complete behavior. We have shown that when four steels, namely, AISI-C1065, AISI-A4063, AISI-C1080, and AISI-C1095, are examined for the effect of martensite on the isothermal transformation of the remaining austenite that there is considerable difference in the accelerating effect of equal amounts of martensite on the austenite to bainite transformations. It is noted that the AISI-C1065 and AISI-A4063 steels and the AISI-C1080 and AISI-C1095 steels are very similar and it is believed that something is happening that at present is not too clear.

### Authors' Reply

The authors wish to thank Dr. Troiano and Mr. Klier for calling attention to the Russian reference. It is, indeed, gratifying to know that the results are in good agreement in most cases.

It is very interesting to note that Dr. Troiano and Mr. Klier found the Ar″ temperature vs. composition curve of chromium steels to deviate from strict linearity at low chromium concentrations, in much the same way as we found for cobalt steels. To explain these effects more precise experimental data are needed on the individual contributing effects on the Ar″ of the alloying elements in very dilute solutions. Such data would have to be obtained by experimental means of far greater precision than the microscopic quench-temper method.

As regards the effect of the presence of martensite in nucleating the bainite reaction, our experimental evidence definitely suggests that immediately below the Ar″ bainite needles make their appearance much sooner than one would expect from a linear extrapolation of the "C" curve. Whether this effect is instrumental in actually increasing the total transformation rate to bainite, both below and above the Ar″, or whether other factors are involved, as suggested by Mr. Elmendorf, must await further experimental study.

# EFFECT OF TIME, TEMPERATURE AND PRIOR STRUCTURE ON THE HARDENABILITY OF SEVERAL ALLOY STEELS

By J. Welchner, E. S. Rowland and J. E. Ubben

*Abstract*

*Five common alloy steels, S.A.E. 4620, NE 9442, S.A.E. 4140, 3240 and 4340 were used in this investigation. The effect of five prior structures, namely, spheroidized, annealed, normalized, hot-rolled, and quenched, on Jominy hardenability over time intervals of 0, 10, 40 minutes and 4 hours at 1525 degrees Fahr. were explored. The effect of a range of quenching temperatures from 1450 to 1600 degrees Fahr. was determined on the annealed and normalized prior structures. End quench curves for the variety of conditions are presented together with summarizing curves to show the effect of the several factors at Rockwell C 50 (Rockwell C 37 for the S.A.E. 4620 type) level of comparison. A few tensile and Izod values were obtained showing the effect of prior structure on physical properties of S.A.E. 4140 and 4340 as related to the hardenability values.*

FOR a great many applications the consumer of constructional alloy steels is definitely interested in an accurate knowledge of the hardenability of the material destined for his heat treating operations. The production hardening of these alloy steel parts is conducted from a multitude of prior structures ranging from completely spheroidized to normalized and in some cases prior quenched. Various proportions of lamellar and spheroidized carbide, depending upon the machinability characteristics desired, are used as starting structures for the hardening operation while some parts are heat treated from a hot-rolled or as-forged prior condition. Again, the time intervals these parts are held at the quenching temperature before

This paper is a condensation of a thesis presented by J. Welchner in partial fulfillment of the degree of metallurgical engineer in the University of Michigan.

A paper presented before the Twenty-fifth Annual Convention of the Society, held in Chicago, October 18 to 22, 1943. Of the authors, J. Welchner is assistant research metallurgical engineer, E. S. Rowland is research metallurgical engineer, and J. E. Ubben is assistant metallurgist in The Steel and Tube Division, The Timken Roller Bearing Company, Canton, Ohio. Manuscript received June 21, 1943.

quenching may vary from a very few minutes in continuous furnace operation to a matter of hours for large parts quenched from batch type furnaces. Finally, quenching temperatures sometimes vary widely in different plants for the same type of steel, depending upon distortion and other local requirements. The quenching temperature variation inherent in production furnace operation from one quenching period to the next and in many large hardening furnaces also must be recognized.

In contrast to this variety of conditions in production, hardenability testing is nearly always carried out under known and rigidly controlled conditions. It is quite general practice to test from a normalized prior structure and to heat for a total time interval of 1 hour. It is true that the quenching temperature used in testing is usually that employed for the part in production, yet the temperature variation is nearly always much less and occasionally hardenability data are available only from a different quenching temperature. The present investigation was inspired by the thought that perhaps the as-quenched hardness traverse of the production part could not be predicted with satisfactory accuracy when the conditions of prior structure, quenching temperature and time at quenching temperature were significantly different from those in effect during the testing procedure.

The general effects of these variables of time, temperature and prior structure on the critical cooling rate and hence hardenability have been known for many years but the published information has been largely qualitative in nature and difficult if not impossible to transpose into terms of quantitative changes in hardenability. To cite only a meager few of many such investigations, as early as 1919 Portevin and Garvin (1)* recognized the influence of initial state and time of heating on the critical cooling rate of carbon steels, Bain (2) quite adequately discussed the maximum rate of austenite transformation during quenching as a function of dissolved elements and other factors, and Lauderdale and Harder (3) have shown the exceedingly short time periods necessary to completely dissolve carbides on heating low and medium carbon steels to temperatures of 1600 degrees Fahr. and above as well as the longer times required at lower temperatures. Mehl (4) found that the diffusion coefficient of carbon was only slightly affected by alloying elements and that the decreasing rate of growth of pearlite on isothermal transformation

*The figures appearing in parentheses refer to the bibliography appended to this paper.

with increasing alloy content, for example, is in no way a function of carbon diffusion rate and can only be explained by the necessity for the diffusion of the alloying elements themselves. Digges (5) showed that hardenability is seriously impaired, under otherwise favorable conditions, by the amount and condition of undissolved carbides remaining at the time of quench. Finally, Williams (6) has presented the only quantitative data of which the authors are aware, showing the effects of the variables under consideration upon hardenability. He published limited information concerning how the factors of quenching temperature, time at quenching temperature, prior structure and the degree of heterogeneity produced variations in hardenability inconsistent with normal expectancy.

In view of this lack of sufficient quantitative information, it was decided to investigate the effects of time at quenching temperature, quenching temperature and prior structure on the hardenability of 5 typical alloy steels of low and medium carbon content. Prior structures were varied from fully spheroidized to oil quenched, times ranging from zero minutes to 4 hours at quenching temperature were employed on all prior structures and the effect of quenching temperature itself was determined for two of the prior structures at constant time and at temperatures from 1450 to 1600 degrees Fahr. (790 to 870 degrees Cent.). The widespread and well deserved popularity of the end quench method of hardenability testing developed by Jominy (7) was an important factor in the choice of this method of determination. Having developed the hardenability relationships, some information was obtained regarding the effects of time and prior structure on the physical properties of two of the medium carbon steels.

## Procedure

One 0.20 and four 0.40 per cent carbon alloy steels were chosen for this investigation. S.A.E. 4620 was selected as typical of the low carbon alloy group while NE 9442 and S.A.E. 4140, 3240 and 4340 were chosen from the medium carbon steels because they represented about the full range of alloy content and hardenability variation. Both electric and open-hearth melting practices are represented in this group, the analyses of which are given in Table I. All material was obtained in the form of hot rolled 1¼-inch diameter bars.

Five prior structures were used in investigating the effect of

**Table I**
**Chemical Analysis**

| Type | Melt | C | Mn | P | S | Si | Cr | Ni | Mo |
|---|---|---|---|---|---|---|---|---|---|
| S.A.E. 4620 | Electric | 0.19 | 0.55 | 0.018 | 0.018 | 0.29 | 0.23 | 1.75 | 0.24 |
| NE 9442 | Open Hearth | 0.43 | 1.15 | 0.013 | 0.018 | 0.45 | 0.25 | 0.30 | 0.11 |
| S.A.E. 4140 | Open Hearth | 0.37 | 0.74 | 0.017 | 0.023 | 0.29 | 1.05 | 0.23 | 0.21 |
| S.A.E. 3240 | Open Hearth | 0.41 | 0.55 | 0.019 | 0.020 | 0.26 | 1.09 | 1.69 | 0.03 |
| S.A.E. 4340 | Electric | 0.38 | 0.65 | 0.019 | 0.016 | 0.27 | 0.71 | 1.56 | 0.39 |

time at quenching temperature on hardenability. These comprised spheroidized, annealed, hot-rolled, normalized, and oil-quenched, and covered the full range of prior structures likely to be used in commercial hardening operations. The spheroidizing was accomplished on short lengths of the hot-rolled bars in a controlled laboratory furnace using cycles which produced uniform, fairly fine spheroidization. The annealed structures were obtained by production mill annealing the hot-rolled bars with other material of the same analysis. Such annealing cycles are designed to produce mixtures of lamellar and spheroidized carbides for optimum machining properties. An exception is the S.A.E. 4620 which was given a typical mill normalize from 1600 degrees Fahr. (870 degrees Cent.). Photomicrographs of the annealed structures are shown in Figs. 1 through 5. Short lengths of hot rolled bars were normalized from 1750 degrees Fahr. (955 degrees Cent.) in the case of the 4620 analysis and from 1650 degrees Fahr. (900 degrees Cent.) in the case of the medium carbon steels. The prior quenched structures were obtained by machining A.S.T.M. end quench specimens, heating them in a "neutral" salt bath to 1550 degrees Fahr. (845 degrees Cent.) and oil quenching. The hot-rolled structures were used as received. The Brinell hardnesses of all steels in all prior structures are given in Table II.

**Table II**
**Brinell Hardnesses of Prior Structures**

| | Type Steel | | | | |
|---|---|---|---|---|---|
| Prior Structure | 4620 | 9442 | 4140 | 3240 | 4340 |
| Spheroidized | 131 | 156 | 152 | 182 | 171 |
| Annealed | 170 | 170 | 170 | 187 | 179 |
| Hot-Rolled | 179 | 262 | 331 | 302 | 285 |
| Normalized | 187 | 255 | 277 | 331 | 311 |
| Oil-Quenched | 285 | 495* | 477* | 578* | 514* |

*By conversion from Rockwell C.

Since it was desired to investigate the effect of time at temperature at short intervals, it was necessary to use a rapid method of heating the hardenability specimens. Consequently, a slightly decar-

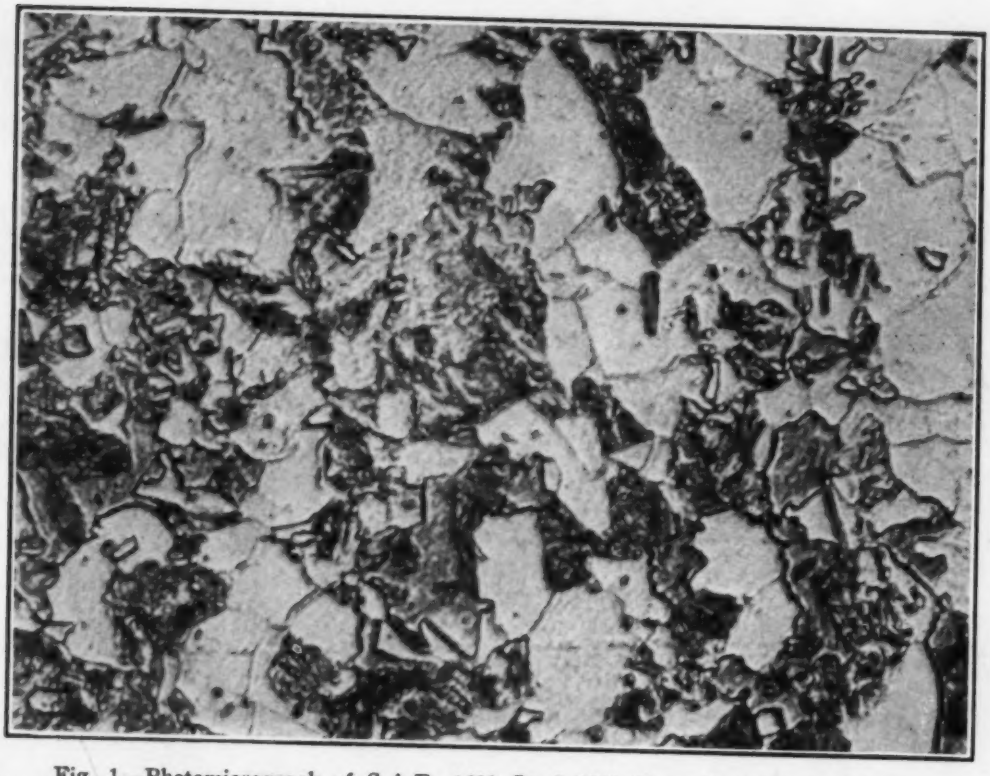

Fig. 1—Photomicrograph of S.A.E. 4620 Steel Mill Normalized from 1600 Degrees Fahr. 170 BHN. × 1000.

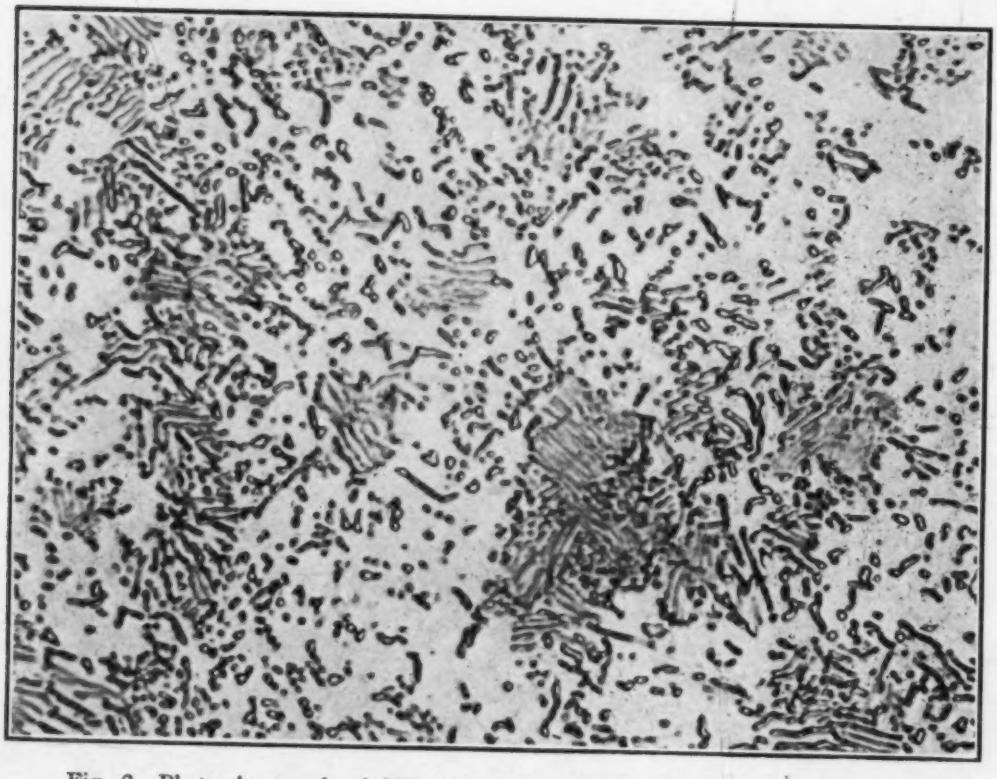

Fig. 2—Photomicrograph of NE 9442 Steel Mill Annealed. 170 BHN. × 1000.

burizing, electrically heated salt bath was chosen after determinations on several steels showed no measurable difference between this method and conventional furnace heating. Preliminary experiments with a dummy specimen, in the exact center of which a thermocouple was welded, indicated that 6 minutes were required for the center of the specimen to reach 1525 degrees Fahr. (830 degrees Cent.). A total time in the salt bath of 6 minutes then represented zero time

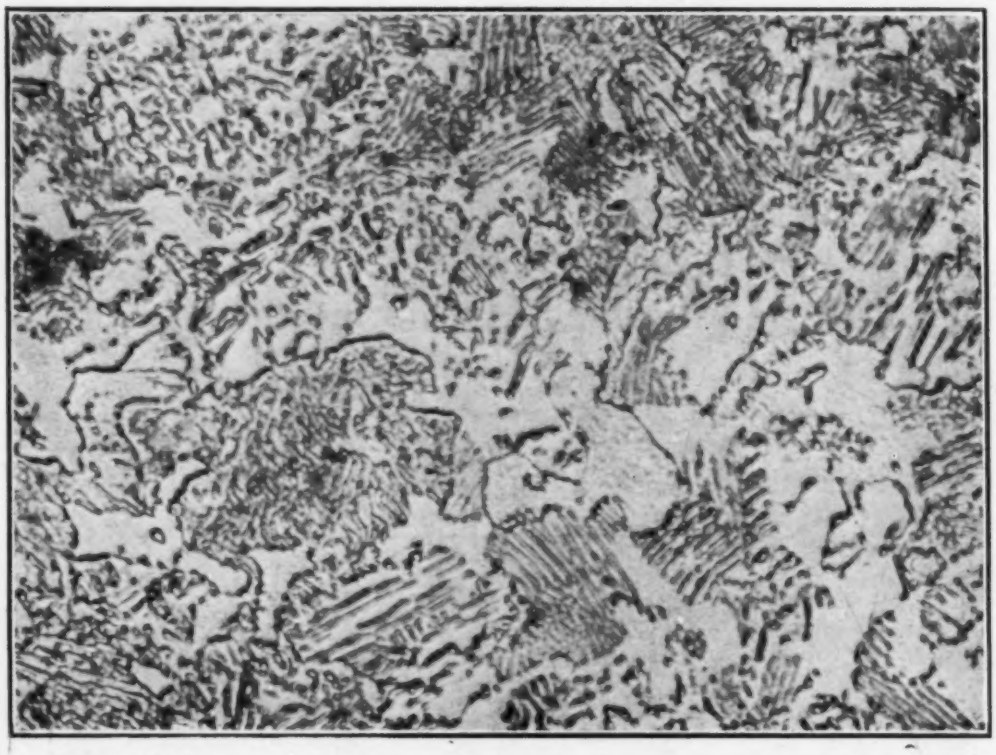

Fig. 3—Photomicrograph of S.A.E. 4140 Steel Mill Annealed. 170 BHN. × 1000.

at temperature. Additional times at quenching temperature of 10 minutes, 40 minutes and 4 hours were chosen, embracing about the total spread of commercial heat treating cycles with the exception of flame and induction hardening. All five prior structures for each steel were explored at a quenching temperature of 1525 degrees Fahr. (830 degrees Cent.).

The procedure employed in determining the effect of varying quenching temperature was only slightly different. A Hump furnace was used to heat the hardenability specimens which were inserted vertically in closely fitting, closed end metal tubes. A few pellets of spent carburizing compound served to prevent scaling over the effective length of the specimen. Preliminary experiments with

dummy specimens here showed that an average of 20 minutes was required for the hardenability specimen to reach the quenching temperatures used. A total heating time of 1 hour was employed for all furnace-heated samples, corresponding to 40 minutes at temperature for the salt bath-heated specimens. Quenching temperatures ranging from 1450 to 1600 degrees Fahr. (790 to 870 degrees Cent.) were examined for each steel from the standpoint of two prior structures—annealed and normalized—except for 4620 which was investigated only in the normalized prior condition and from an additional temperature of 1700 degrees Fahr. (925 degrees Cent.).

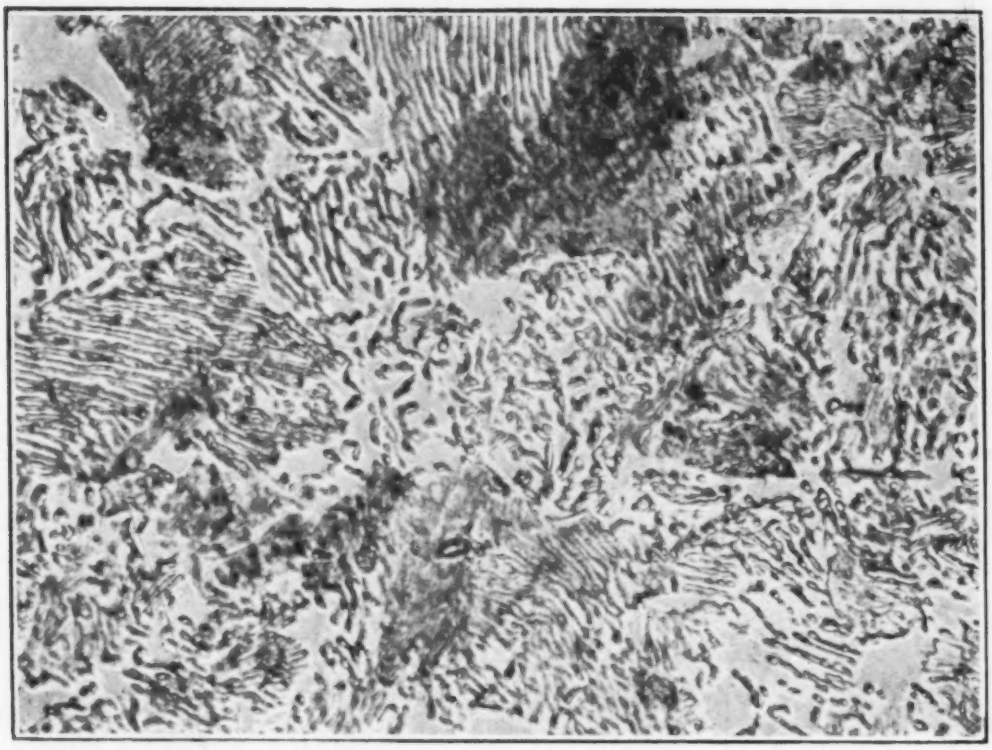

Fig. 4—Photomicrograph of S.A.E. 3240 Steel Mill Annealed. 187 BHN. × 1000.

With the above exceptions, the standard A.S.T.M. end quench hardenability testing procedure was employed throughout this work. Collar-type end quench hardenability specimens were machined from all prior structures except for those which were machined before oil quenching. All conditions were tested in duplicate and Rockwell C hardnesses taken on two 0.015 inch flats per specimen. The four sets of readings for each determination were averaged and the results plotted as curves of Rockwell C hardness versus distance from the quenched end. The curves presented herein were so drawn that no

average value deviated by more than 1 point Rockwell from the curve.

Since some of the times and temperatures employed were well beyond the normal values used in hardenability testing, the extent of decarburization was carefully investigated. The total depth of any microscopically visible carbon depletion on the salt bath heated specimens did not exceed 0.013 inch for the 4-hour prior quenched specimens and was barely noticeable at 40 minutes. Since hardness values

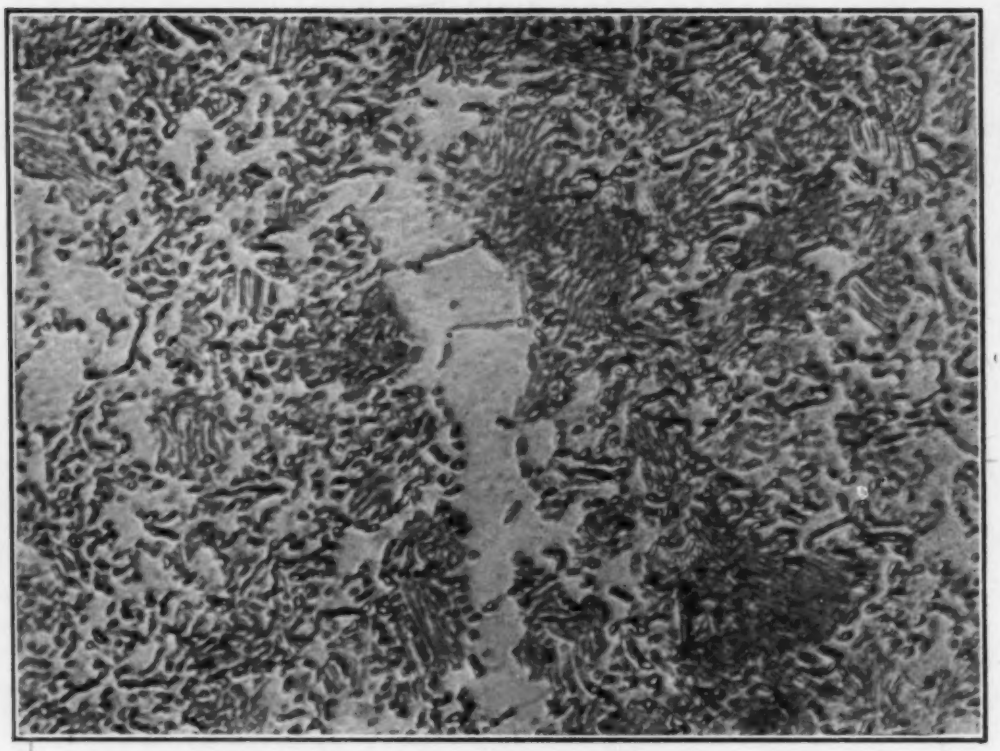

Fig. 5—Photomicrograph of S.A.E. 4340 Steel Mill Annealed. 179 BHN. × 1000.

taken at both 0.015 and 0.030 inch depths on negligibly decarburized specimens checked exactly, 0.030 inch flats were ground on the 4-hour time specimens to avoid any possibility of decarburization effects. Specimens furnace-heated a total time of 1 hour at 1600 degrees Fahr. (870 degrees Cent.) failed to reveal more than 0.005 inch depth of carbon depletion, hence the hardness values obtained at 0.015 inch depths were considered satisfactory.

Oxidation grain size values were obtained for all steels, using the time intervals and temperatures chosen for this work. Since no measurable difference could be found over this wide range of conditions, grain size is not considered as a factor in this investigation.

The procedure employed in investigating the effect of time at

temperature on the physical properties of 4140 and 4340 was much the same as that employed for the corresponding hardenability determinations. Both normalized and annealed prior structures were examined, the former at total heating times in the salt bath of 10 minutes and 4 hours and the latter at 10 minutes, 40 minutes and 4 hours. Duplicate oversize tensile and 3 notch Izod specimens were machined, oil-quenched from 1525 degrees Fahr. (830 degrees Cent.), tempered to 29-31 Rc and finished. Dummy specimens of each condition and the same size were quenched at the same time and sectioned for as-quenched and tempered hardnesses.

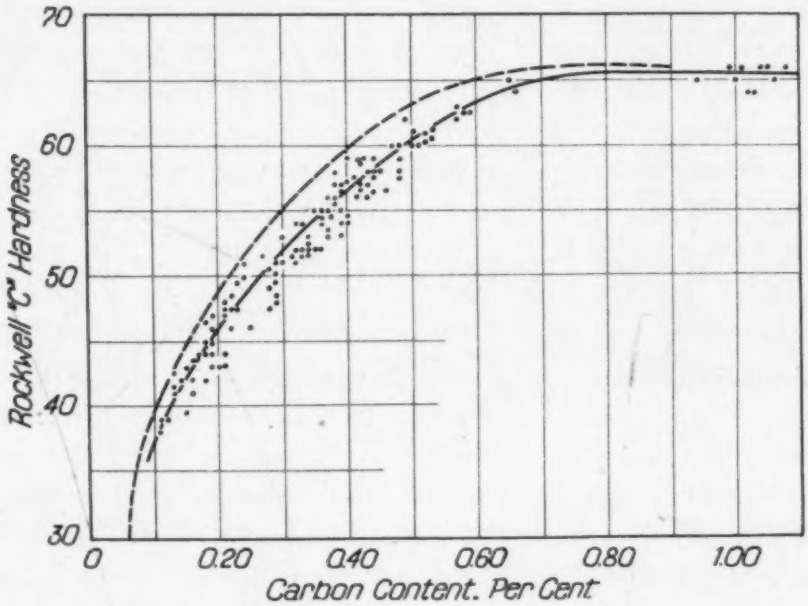


Fig. 6—Effect of Carbon Content on the Maximum Hardness Obtained on the Jominy Specimen.

## Presentation of Results

Before attempting a detailed presentation of the results of this investigation, a few general points need clarification. First, distance from the quenched end of the specimen to 50 Rockwell C was chosen as the criterion of hardenability, in accordance with S.A.E. recommended practice, except in the case of S.A.E. 4620 where the distance to 37 Rockwell C was used, a hardness corresponding very closely to the 50 per cent martensite point. Next, the term "maximum hardness" is used in this paper to designate the highest hardness value attained on the longitudinal flat of the Jominy specimen, usually the

first sixteenth, rather than the highest hardness the analysis is capable of attaining. The relationship between these two values as a function of carbon content is shown in Fig. 6. The dotted line represents the highest hardness attainable at the carbon content shown and was taken from the work of Burns, Moore and Archer (8). The plotted points represent the highest hardnesses found in the end quench hardenability testing of a large number of alloy steels in the authors' laboratory. The solid line represents a weighted average through these points. Since most of the errors encountered in obtaining these values tend to produce low results, the curve was drawn slightly higher than the arithmetic mean. It can be seen that the curves are practically parallel but converge at both low and high carbon contents.

Finally, a satisfactory interpretation of the data presented requires a knowledge of the reproducibility of results—that is, the experimental error. Some of the variations in hardenability shown are quite small and hence this error must be taken into account. Analysis of the results obtained on individual specimens, which were averaged to arrive at the curves shown, indicated that the experimental error was about $\frac{1}{32}$ inch at 50 Rockwell C, slightly less at low hardenability values and slightly greater for high hardenability steels. For the purpose of practical application of the results, however, hardenability changes less than $\frac{1}{16}$ inch in amount are considered negligible.

The effects shown and the conclusions drawn must be considered as being applicable only to the particular heats of steel investigated. While it is believed that the heats used are typical of the type analysis, additional heats of the same types of steel have not been examined.

## *S.A.E. 4620*

The hardenability curves of Fig. 7 show the effect of four time periods at 1525 degrees Fahr. (830 degrees Cent.) from 5 prior structures. It should be borne in mind that the curves designated "A" represent a mill normalize from 1600 degrees Fahr. (870 degrees Cent.) and not a true annealing treatment in this case, although it will be so called. At zero time at temperature, both the maximum hardness and hardenability of the spheroidized and annealed prior structures are low while the other three structures produced higher and practically identical maximum hardness and hardenability results. The reason for this behavior was confirmed by microscopic examina-

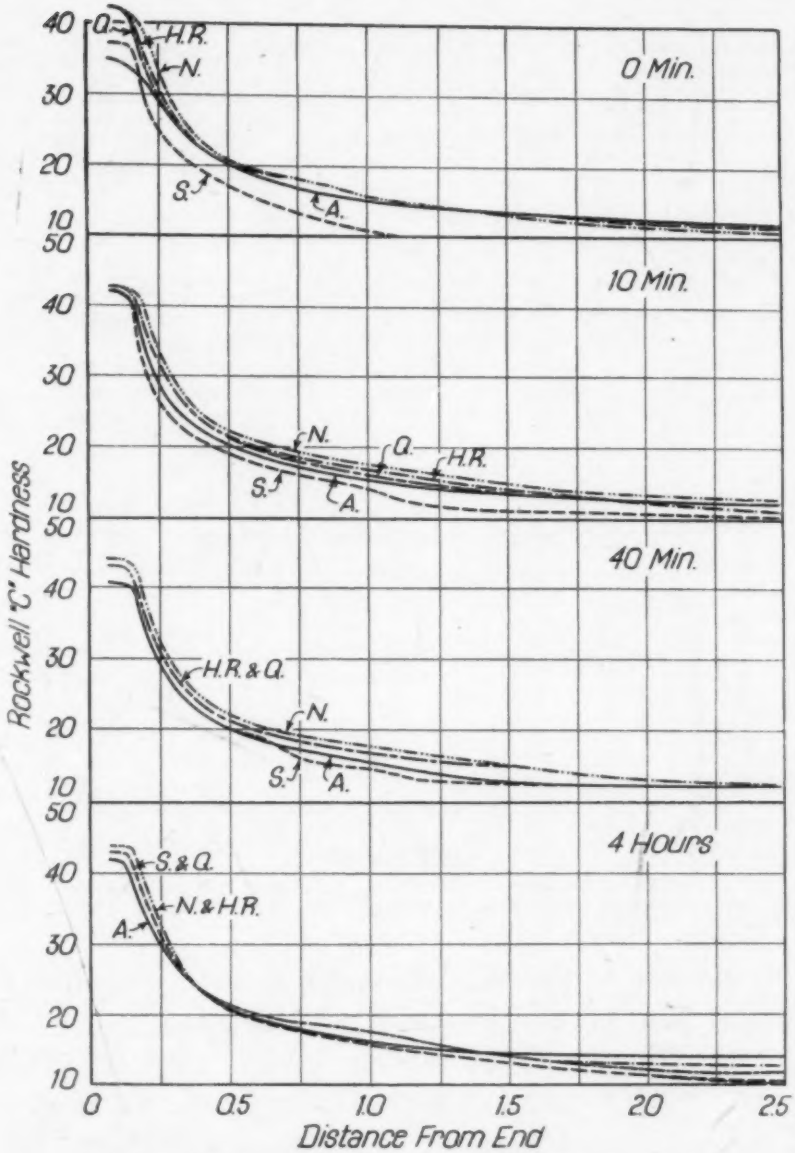


Fig. 7—Effect of Time at 1525 Degrees Fahr. on the Hardenability of S.A.E. 4620 from 5 Prior Structures.

tion of the individual hardenability specimens in the region of the first Rockwell reading. Both the annealed and spheroidized prior condition specimens contained free ferrite at the quenched end while the remaining 3 sets did not.

After 10 minutes at temperature, the maximum hardnesses are identical and the hardenability curves much closer together, although the spheroidized and annealed conditions still produce slightly lower results. None of the microstructures showed any traces of ferrite at the quenched end. At 40 minutes all hardenability results are substantially identical, yet the two slower cooled prior structures are

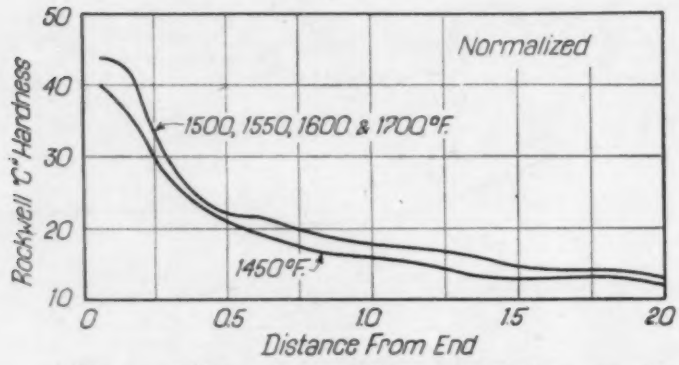


Fig. 8—Effect of Quenching Temperature on the Hardenability of S.A.E. 4620 from a Normalized Prior Structure.

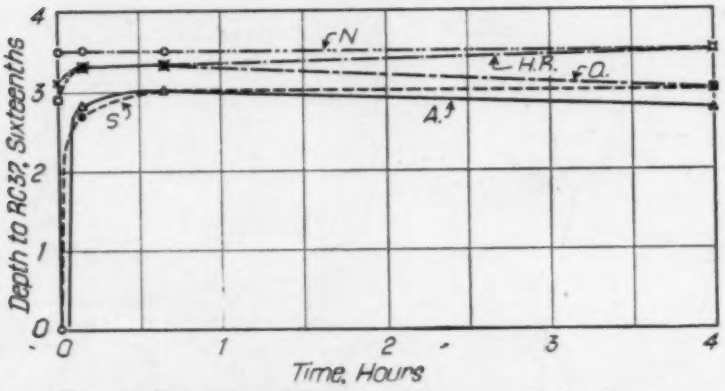


Fig. 9—Summary of Effects of Time and Prior Structure on Hardenability of S.A.E. 4620.

still on the low side of the narrow spread of results. After 4 hours at temperature, all curves are considered identical.

Fig. 8 contains the hardenability curves obtained by varying the quenching temperature of the prior normalized material, time at temperature being constant at 40 minutes. All temperatures from 1500 to 1700 degrees Fahr. (815 to 925 degrees Cent.) inclusive produced identical results, only the 1450 degrees Fahr. (790 degrees Cent.) quench causing low maximum hardness and hardenability due to ferrite retention. This is not surprising since 1450 degrees Fahr. (790 degrees Cent.) is below the $Ac_3$ temperature of this analysis.

A summary of the effects of time and prior structure are given in Fig. 9 in which the depth to 37 Rockwell C on a greatly expanded scale is plotted against time. The low hardenability values of the slower cooled prior structures after short intervals at quenching temperature can be readily seen. Except for these two sets of results and the value obtained on quenching from 1450 degrees Fahr. (790

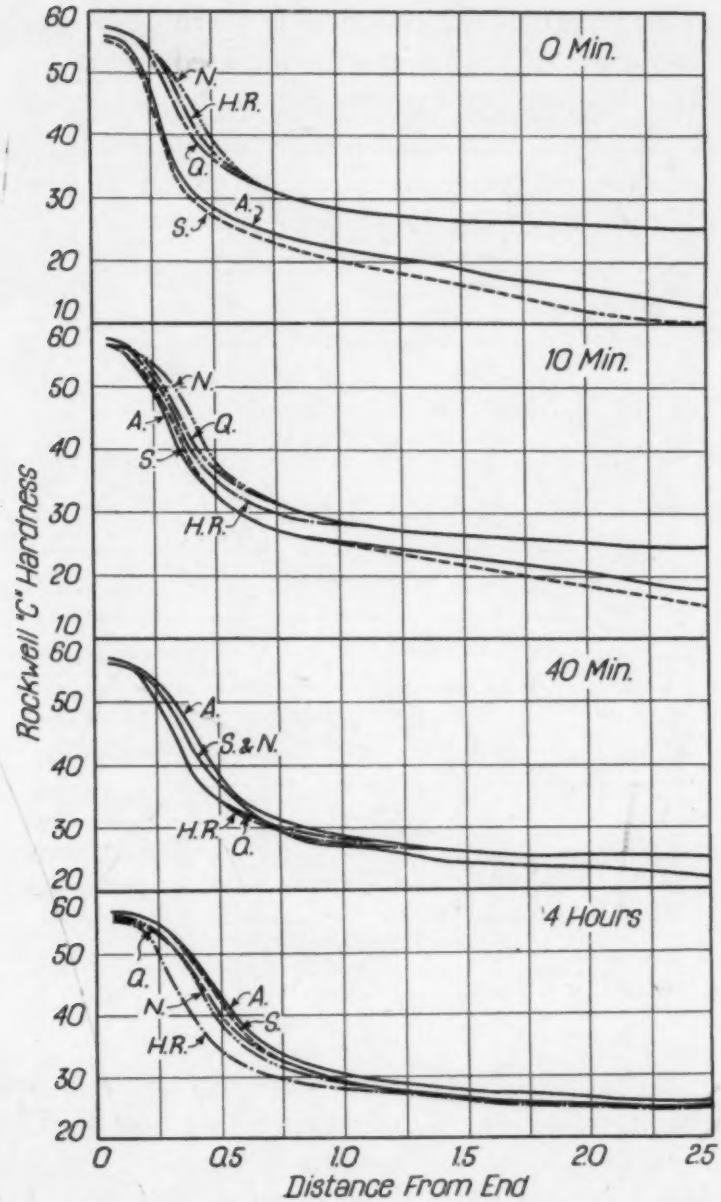


Fig. 10—Effect of Time at 1525 Degrees Fahr. on the Hardenability of NE 9442 from 5 Prior Structures.

degrees Cent.), S.A.E. 4620 can be considered substantially insensitive to changes in the conditions investigated.

## *NE 9442*

The hardenability results obtained on this analysis from the 5 prior structures after the four time intervals at 1525 degrees Fahr. (830 degrees Cent.) are shown in Fig. 10. Spheroidized and

annealed prior structures yielded low hardenability results at zero time at temperature while the low maximum hardnesses developed were found by microscopic examination to be due to the presence of globular carbides, indicating incomplete solution. Normalized, hot-rolled and quenched prior conditions produced substantially equal results and higher maximum hardnesses, confirmed by the complete absence of carbide in the quenched structure. After 10 minutes at

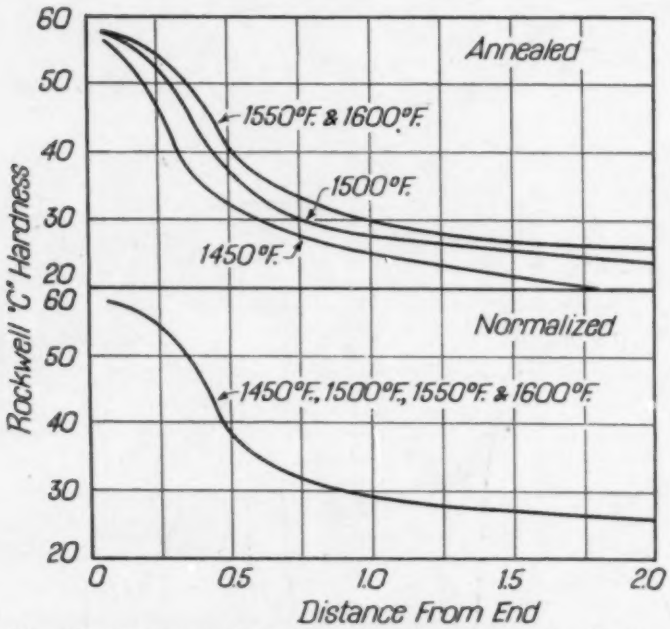


Fig. 11—Effect of Quenching Temperature on the Hardenability of NE 9442 from 2 Prior Structures.

temperature, the hardenability curves are brought much closer together but the two slowly cooled prior structures are still on the low side. Carbon solution is substantially complete from these two prior conditions at this time interval since only a few scattered carbides could be seen in the quenched structures. With the exception of the 4-hour hot-rolled results, which are unaccountably low, the curves for all prior structures remain closely grouped at the two longer time periods.

The effect of quenching temperatures from 1450 to 1600 degrees Fahr. (790 to 870 degrees Cent.) on annealed and normalized NE 9442 is shown in Fig. 11. From the annealed condition, a small but definite increase in hardenability occurs with increase in temperature up to 1550 degrees Fahr. (845 degrees Cent.) with no further increase to 1600 degrees Fahr. (870 degrees Cent.). The various

quenching temperatures employed from the normalized condition produced identical results.

The effects of these variables are summarized in Figs. 12 and 13 in which depth to 50 Rockwell C is plotted as a function of time and temperature, respectively. It can be seen from Fig. 12 that while the slowly cooled prior structures show a slight increase in hardenability with time and the rapidly cooled ones tend to decrease

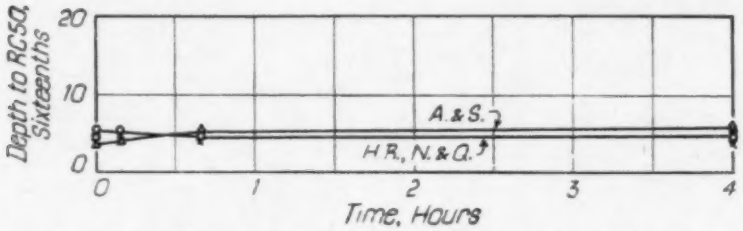


Fig. 12—Summary of Effects of Time and Prior Structure on the Hardenability of NE 9442.

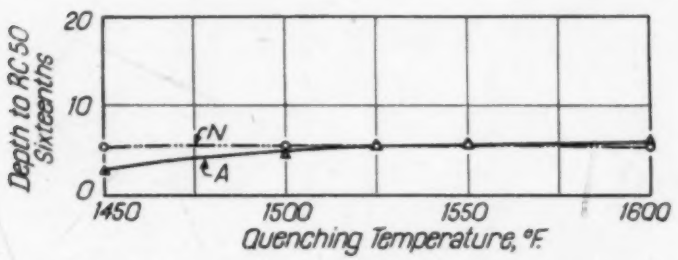


Fig. 13—Summary of Effects of Temperature and Prior Structure on the Hardenability of NE 9442.

just as slightly, the effect of time is small beyond extremely short time at temperature periods for even the slowly cooled prior conditions. In regard to temperature variation, only the slowly cooled prior structure at 1450 and 1500 degrees Fahr. (790 and 815 degrees Cent.) shows any significant variation from otherwise substantially constant values. In Fig. 13, as in steels considered later, the values at 1525 degrees Fahr. (830 degrees Cent.) are those obtained in the study of effect of time at 40 minutes at temperature.

## *S.A.E. 4140*

Fig. 14 shows the hardenability changes occurring at the four time intervals from the five prior structures in S.A.E. 4140 steel. At zero time at temperature tremendous differences in both maximum hardness and hardenability obtain between the slowly and rapidly cooled prior structures. On microscopic examination, the quenched end of the previously spheroidized specimen contained a large amount

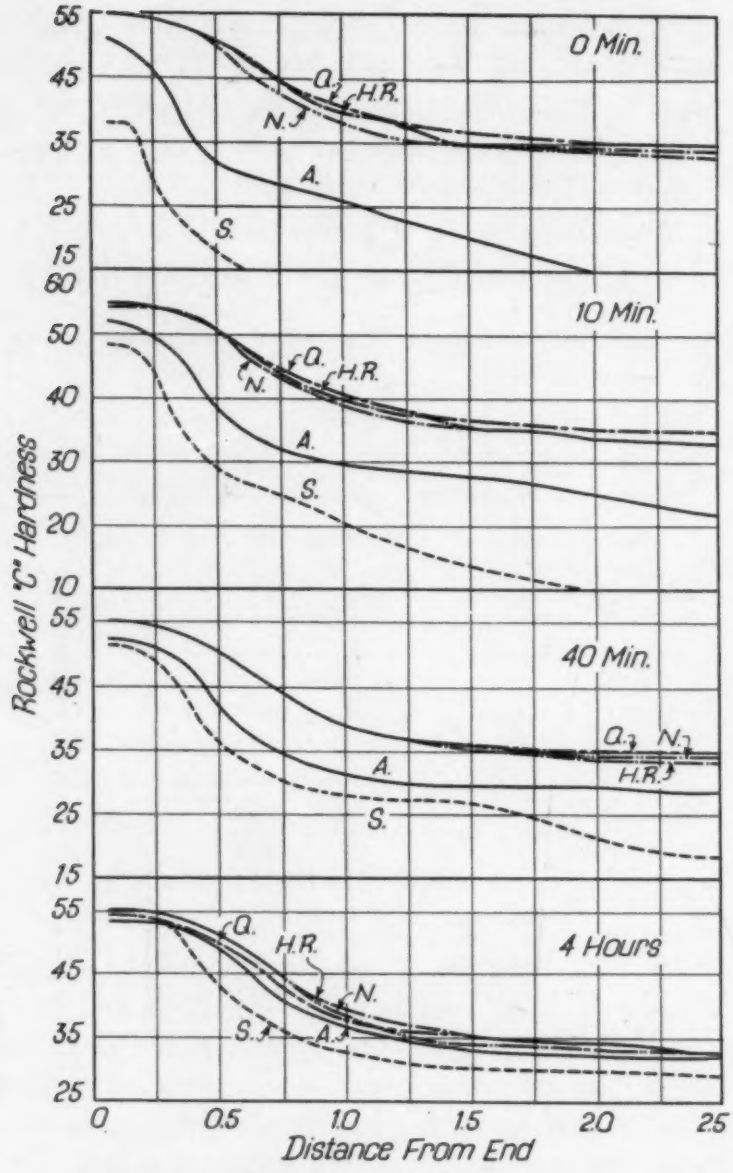


Fig. 14—Effect of Time at 1525 Degrees Fahr. on the Hardenability of S.A.E. 4140 from 5 Prior Structures.

of globular carbides and 25 per cent ferrite while the annealed specimen was free from ferrite but much carbide was present. The three rapidly cooled prior structures were wholly martensitic and substantially equal in hardenability.

After 10 minutes at temperature, the hardenability values and maximum hardnesses are improved but both are still quite inferior to the rapidly cooled prior structure results. The structure of the spheroidized specimen contains small amounts of both ferrite and quenching pearlite together with considerable carbide. With further

increase in time at temperature the curves for the two slowly cooled conditions slowly approach the others. After 4 hours at temperature, the hardenability from the annealed condition has almost reached the substantially equal values found for the hot-rolled, normalized, and quenched prior structures while that from the spheroidized condition is still low. Only at this time interval do maximum hard-

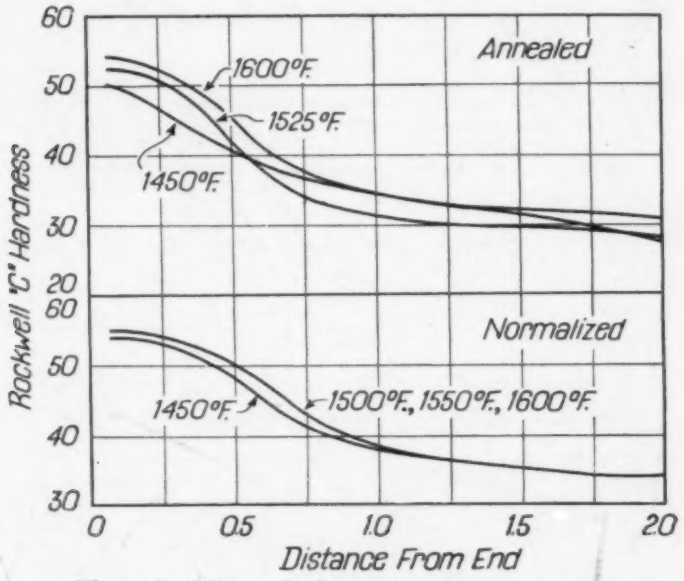


Fig. 15—Effect of Quenching Temperature on the Hardenability of S.A.E. 4140 from 2 Prior Structures.

nesses for these two conditions reach normal values for this analysis. Occasional elongated carbides were noticed in the quenched structure of the prior annealed specimen while small amounts were still present in the spheroidized.

The influence of quenching temperature on the hardenability of this analysis from the annealed and normalized conditions is shown in Fig. 15. From an annealed prior structure, a steady increase in hardenability and maximum hardness is noted at the three increments of temperature shown. As confirmed by the presence of carbide in the structure, full solution is still slightly incomplete after 40 minutes at 1600 degrees Fahr. (820 degrees Cent.). By contrast, the hardenability increase from 1450 to 1500 degrees Fahr. (790 to 815 degrees Cent.) with the normalized prior structure is small and no further increase occurs over the temperature range examined.

These effects are summarized for time and temperature in Figs. 16 and 17, respectively. It is apparent that the effect of time on the hot-rolled, normalized and quenched prior conditions is negligible as

is the difference among them except at the 4-hour period, and even here it is small. The two slowly cooled prior structures behave alike, the annealed showing less change than the spheroidized but both showing large variations with time. The substantial difference in hardenability from normalized and annealed prior conditions at all quenching temperatures is shown in Fig. 17. It is significant that

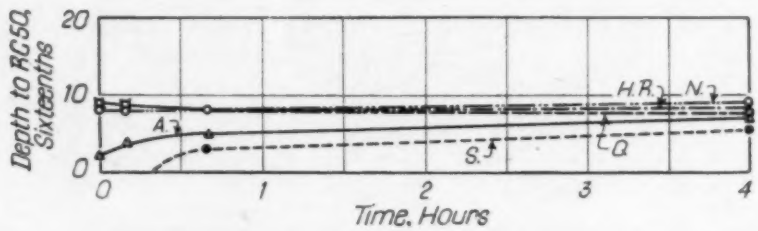


Fig. 16—Summary of Effects of Time and Prior Structure on the Hardenability of S.A.E. 4140.

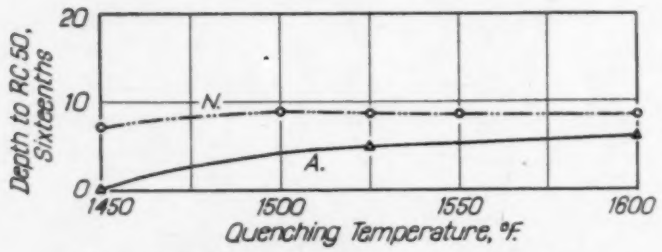


Fig. 17—Summary of Effects of Temperature and Prior Structure on the Hardenability of S.A.E. 4140.

40 minutes at 1600 degrees Fahr. (870 degrees Cent.) from an annealed structure does not equal the hardenability produced after the same time at 1450 degrees Fahr. (790 degrees Cent.) from the normalized state and the latter value is lower than the balance of the normalized results. This analysis must be considered as substantially insensitive to time and temperature variations from rapidly cooled prior structures and from above the $Ac_3$ temperature but subject to tremendous changes when treated from annealed or spheroidized structures.

## *S.A.E. 3240*

The influence of time on this steel, shown in Fig. 18, follows the same general pattern of behavior as S.A.E. 4140 previously considered. At zero time the spheroidized and annealed prior conditions fall far below the equal hardenability values obtained from the three rapidly cooled prior structures. Carbon solution is not complete as evidenced by low maximum hardness and the carbides present

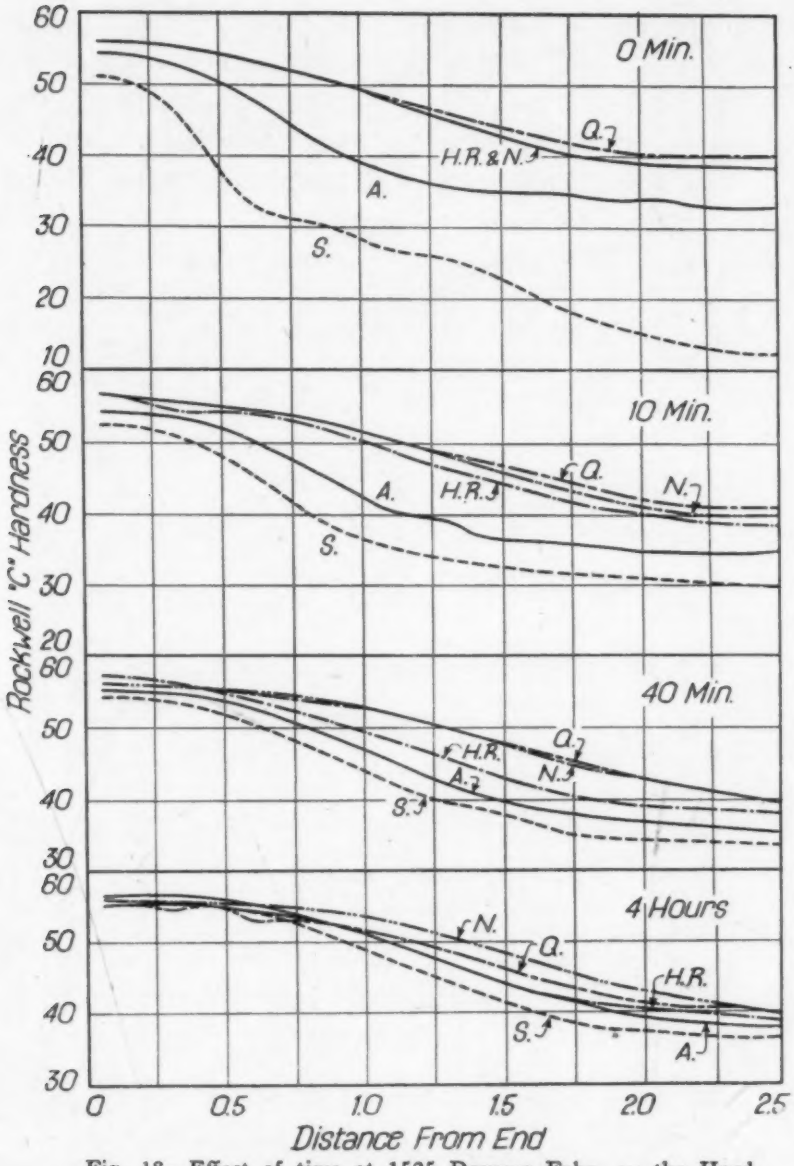


Fig. 18—Effect of time at 1525 Degrees Fahr. on the Hardenability of S.A.E. 3240 from 5 Prior Structures.

in the microstructure, while complete solution exists from the three rapidly cooled conditions. Increase in time raises the hardenability from the two slowly cooled conditions but again the spheroidized prior structure never attains the same hardenability range as the rest while the annealed barely reaches the low limit of the range covered by the rapidly cooled group. Complete carbon solution is reached only at 4 hours from the coarse carbide prior conditions and occasional small carbides can be found even after this time in the prior spheroidized specimen. Much more variation among the hot-rolled, normalized and quenched prior structures is present here

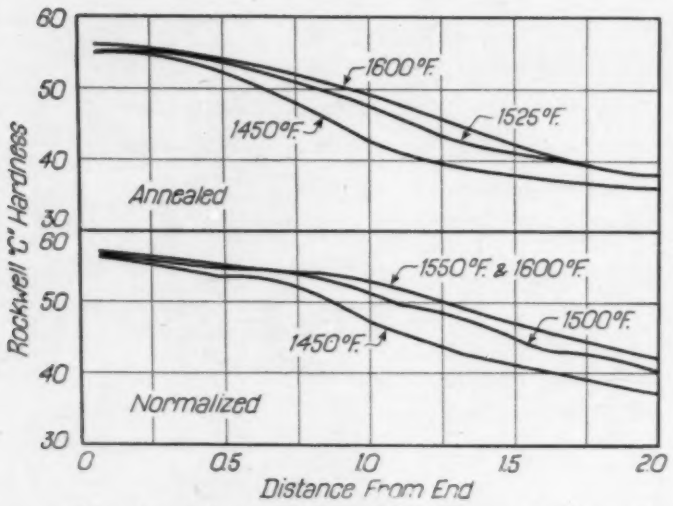


Fig. 19—Effect of Quenching Temperature on the Hardenability of S.A.E. 3240 from 2 Prior Structures.

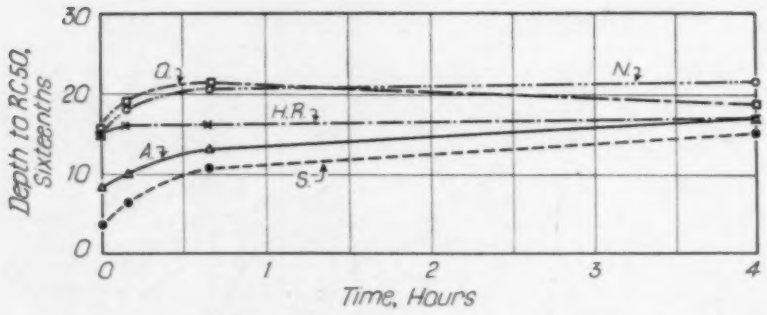


Fig. 20—Summary of Effects of Time and Prior Structure on Hardenability of S.A.E. 3240.

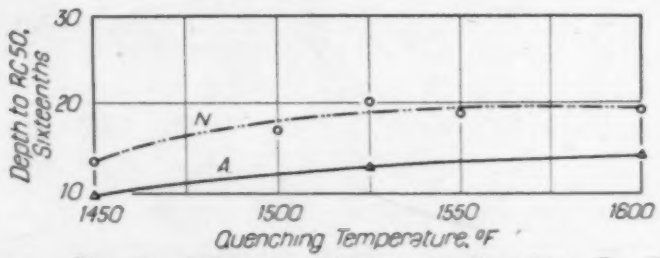


Fig. 21—Summary of Effects of Quenching Temperature and Prior Structure on the Hardenability of S.A.E. 3240.

than for S.A.E. 4140 at all but the shortest time investigated.

The result of increasing the quenching temperature from annealed prior structures (Fig. 19) is a steady increase with temperature over the range studied. Carbide solution is not complete even after 40 minutes at 1600 degrees Fahr. (870 degrees Cent.) as shown by structural observations. When the normalized state is considered, the same general trend is noted up to 1550 degrees Fahr.

(845 degrees Cent.) with no change at 1600 degrees Fahr. (870 degrees Cent.). Carbon solution was found to be complete at all temperatures.

The overall effects of time and prior structure (Fig. 20) again show that the prior structures may be divided into two groups by their behavior, although the difference is not so marked as in S.A.E. 4140. Here, only the hot-rolled prior structure is independent of time, while the normalized and quenched conditions show relatively small but definite increases up to 40 minutes and the quenched shows

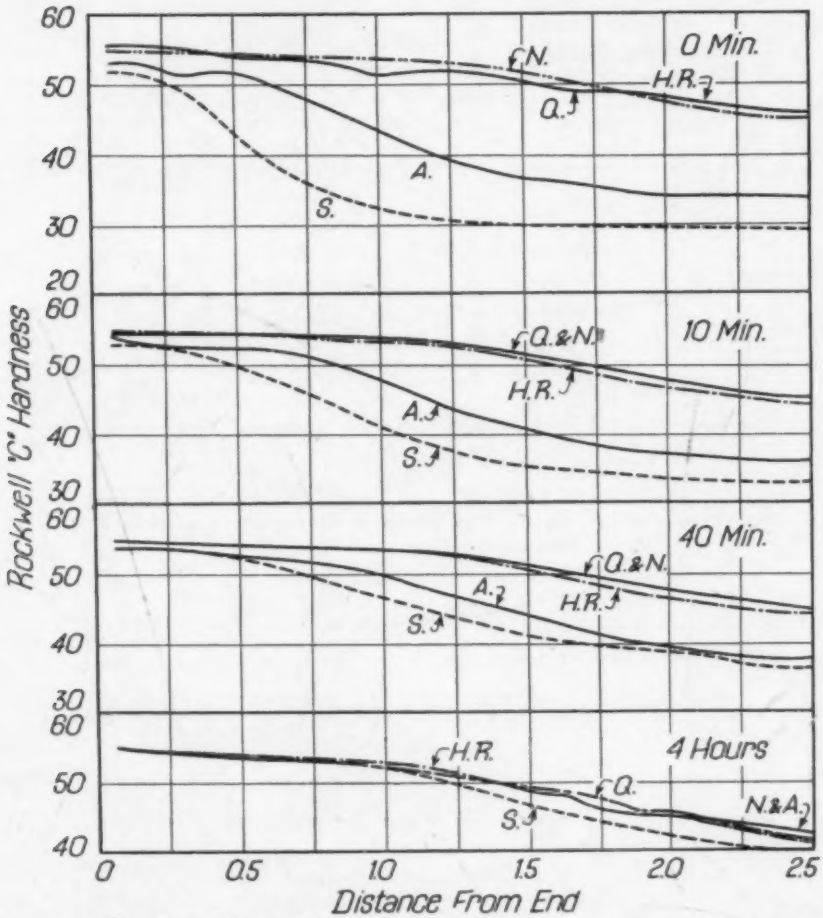


Fig. 22—Effect of Time at 1525 Degrees Fahr. on the Hardenability of S.A.E. 4340 from 5 Prior Structures.

an actual decrease at 4 hours. This last point was re-run and confirmed. Considering the comparative results of quenching temperature and initial condition (Fig. 21), the normalized state produces much higher hardenability at all temperatures, being substantially constant above 1525 degrees Fahr. (830 degrees Cent.). Again, 40 minutes at 1600 degrees Fahr. (870 degrees Cent.) from the annealed

state barely attains the hardenability that is produced from normalized samples quenched from 1450 degrees Fahr. (790 degrees Cent.) after equal time at temperature.

## *S.A.E. 4340*

The hardenability curves for the various time intervals at 1525 degrees Fahr. (830 degrees Cent.) (Fig. 22) show the same

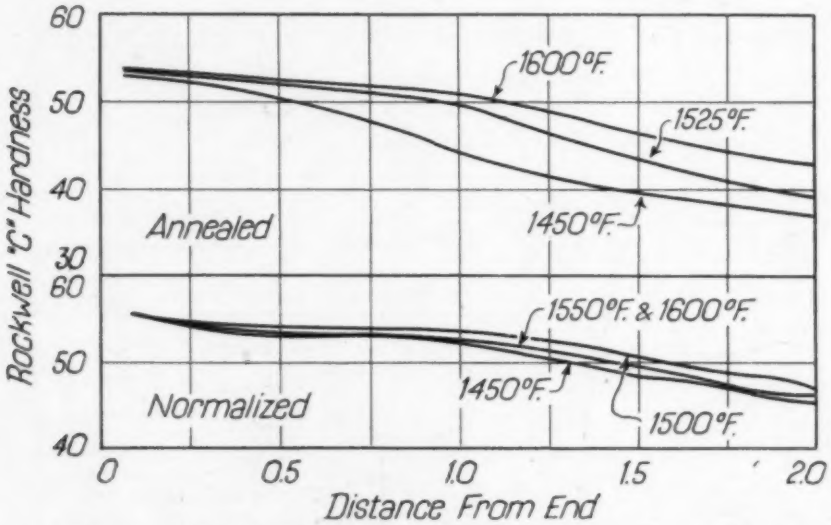


Fig. 23—Effect of Quenching Temperature on the Hardenability of S.A.E. 4340 from 2 Prior Structures.

general behavior as was observed previously. The same tremendous difference in hardenability between the prior annealed and spheroidized and the prior hot-rolled, normalized and quenched was obtained at short times. In spite of the low hardenability, the maximum hardnesses of the previously slowly cooled group are almost equal to the others, confirmed by the quite small amounts of carbide in the quenched microstructure. The numbers of these carbides decrease gradually with increasing time, having virtually disappeared in the annealed after 40 minutes at temperature and in the spheroidized after 4 hours. There is a corresponding increase in hardenability from these two initial conditions with time until at 4 hours the annealed becomes coincident with the other group but the spheroidized still lags behind. Here again, some increase in hardenability is noted after carbon solution is visibly complete.

Fig. 23 shows the relationship of prior structure to quenching temperature. From the annealed state, hardenability increases steadily

with quenching temperature while from the normalized condition the greatest variation occurs between 1450 and 1500 degrees Fahr. (790 and 815 degrees Cent.) and the two higher temperatures produce an equal decrease in this value. No ferrite was observable after the time interval used (40 min.) at any temperature or prior structure.

The summarized effects of time and prior structure of Fig. 24 indicate the vast difference between the slowly and rapidly cooled

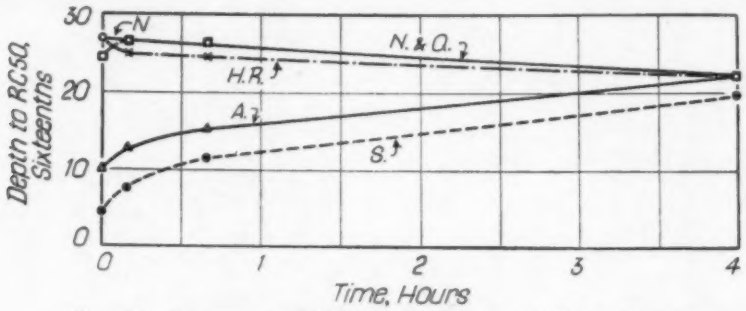


Fig. 24—Summary of Effects of Time and Prior Structure on the Hardenability of S.A.E. 4340.

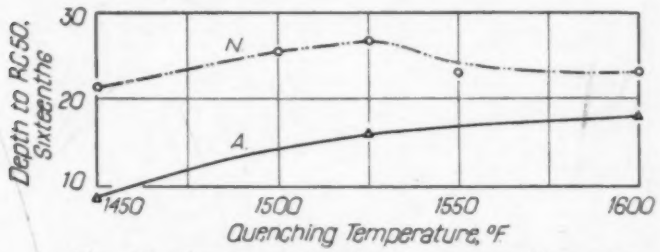


Fig. 25—Summary of Effects of Quenching Temperature and Prior Structure on the Hardenability of S.A.E. 4340.

prior structures. The maximum hardenability with the latter group is obtained at short times and decreases progressively with increasing time. The composite effects of temperature and prior structure (Fig. 25) also show a great difference between the two types of prior structure investigated. The normalized experiences a maximum at 1525 degrees Fahr. (830 degrees Cent.). A tendency toward this same effect was noted for S.A.E. 3240 (Fig. 21) but the extent was so small that it was ignored. Again, the annealed prior structure quenched from 1600 degrees Fahr. (870 degrees Cent.) does not equal any of the normalized hardenability values.

### *Physical Properties*

The results of the limited investigation made to determine the

**Table III**

**Influence of Time and Prior Structure on Physical Properties. Tensiles treated in .575" diameter. Izods treated in .450" square**

| Tempering Temperature | Time at Quench Temp. | Yield Point | Ultimate | Elong. | Red. Area | Izods | Rockwell C Surface | Rockwell C Center | As-Quenched Rc Hardness Surface | As-Quenched Rc Hardness Center |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | **S.A.E. 4140 Normalized** | | | | | | |
| 1100° F. | 10 Min. | 135,000 | 142,500 | 20.0 | 64.3 | 70, 74, 71 | 29 | 30 | 52.5 | 52.5 |
| 1100° F. | 10 Min. | 135,000 | 143,500 | 19.5 | 65.3 | .... | .. | .. | .. | .. |
| 1100° F. | 4 Hours | 135,000 | 143,500 | 20.0 | 63.9 | 73, 69, 72 | 30 | 30.5 | 51.5 | 51.5 |
| 1100° F. | 4 Hours | 135,000 | 148,200 | 18.5 | 63.7 | .... | .. | .. | .. | .. |
| | | | | **Commercial Annealed** | | | | | | |
| 1050° F. | 10 Min. | 138,100 | 145,000 | 17.5 | 60.3 | 56, 60, 57 | 29 | 30.5 | 50 | 50 |
| 1050° F. | 10 Min. | 136,100 | 144,400 | 18.0 | 60.6 | .... | .. | .. | .. | .. |
| 1050° F. | 40 Min. | 143,100 | 150,000 | 18.0 | 62.0 | 58, 60, 58.5 | 30 | 30 | 50 | 50 |
| 1050° F. | 40 Min. | 140,000 | 149,700 | 18.0 | 62.0 | .... | .. | .. | .. | .. |
| 1100° F. | 4 Hours | 135,000 | 146,500 | 18.5 | 63.8 | 64, 68, 67 | 29.5 | 30 | 52 | 52 |
| 1100° F. | 4 Hours | 137,000 | 144,500 | 20.0 | 64.0 | .... | .. | .. | .. | .. |
| | | | | **S.A.E. 4340 Normalized** | | | | | | |
| 1140° F. | 10 Min. | 145,000 | 150,000 | 18.5 | 61.7 | 69, 68, 74 | 29.5 | 29.5 | 52.5 | 52.5 |
| 1140° F. | 10 Min. | 145,000 | 151,000 | 18.5 | 63.2 | .... | .. | .. | .. | .. |
| 1140° F. | 4 Hours | 145,000 | 150,000 | 19.0 | 62.5 | 68, 73, 72 | 30 | 29.5 | 52.5 | 52.5 |
| 1140° F. | 4 Hours | 145,000 | 150,000 | 18.5 | 62.5 | .... | .. | .. | .. | .. |
| | | | | **Commercial Annealed** | | | | | | |
| 1085° F. | 10 Min. | 139,000 | 145,500 | 18.0 | 59.9 | 52, 55, 54 | 30 | 30 | 52 | 52.5 |
| 1085° F. | 10 Min. | 142,500 | 147,000 | 18.0 | 59.7 | .... | .. | .. | .. | .. |
| 1115° F. | 40 Min. | 139,000 | 142,500 | 19.0 | 62.5 | 60, 62, 61 | 30 | 30 | 52.5 | 52.5 |
| 1115° F. | 40 Min. | 141,500 | 143,500 | 19.0 | 61.7 | .... | .. | .. | .. | .. |
| 1135° F. | 4 Hours | 139,500 | 144,500 | 19.5 | 63.7 | 69, 70, 71.5 | 30 | 30 | 53 | 52.5 |
| 1135° F. | 4 Hours | 141,500 | 144,500 | 20.0 | 64.9 | .... | .. | .. | .. | .. |

possible effects of time at temperature and prior structure on the physical properties of S.A.E. 4140 and 4340 are given in Table III. It must be borne in mind that all tests were quenched in such a section size that all conditions produced complete hardening as evidenced by the surface and center, as-quenched and tempered hardnesses.

An inspection of the data discloses that the normalized prior structures of both steels produce properties independent of time at temperature within the range investigated. On the other hand, the annealed prior states of both analyses yield ductility and impact values which show a steadily increasing trend with increase in time at tempering temperature at constant ultimate strength. An increase in tempering temperature was necessary in order to maintain constant hardness at the longer time intervals.

## General Discussion

Since the authors are somewhat more interested in the practical aspects of the above results, no determined attempts were made to obtain sufficient additional evidence in order to offer a theoretical explanation of all the hardenability changes encountered. From a general standpoint, however, sufficient information is at hand to adequately explain some of the effects encountered while we can only hint at the explanation for others.

In the first place, the extremely large differences in hardenability observed at short intervals of time at temperature from the several prior structures for some of the steels is obviously due to the varying rate of carbon solution from the different initial states. The hardenability values obtained from the prior structures at short times for a given steel arrange themselves quite readily in the order of increasing area to volume ratio of the carbide in the prior structure. By this reasoning, for a given amount of carbide, the spheroidized structure should have the slowest solution rate, the annealed next, with the hot-rolled, normalized and quenched structures having the fastest rates of solution. This is borne out by the results obtained, although the differences among the three rapidly cooled prior structures are often too small for measurement. As the alloy content of the steel increases, the spread in hardenability values between the spheroidized and the rapidly cooled prior structures at short times at temperature also increases. This must be due either

to increased resistance to solution of the complex alloy carbides (principally chromium and molybdenum) or to the necessity for diffusion of the alloying elements in the carbides for solution to continue, or both. This also explains the much slower rate of hardenability increase with time from spheroidized and annealed prior structures. Incomplete carbon solution is itself a cause of low hardenability since carbides present in austenite at the moment of quenching serve to nucleate its decomposition and hence increase the critical cooling rate.

Evidence has been found which indicates that in some cases increases in hardenability result from longer holding times after carbon solution is apparently complete, at least from the standpoints of maximum hardness and microscopic examination. This condition must be due either to the presence of carbides too small for microscopic identfication or additional time is necessary for diffusion of the alloying elements in the carbides after solution to produce homogeneous austenite grains. Without any direct evidence, the authors lean toward the latter explanation because maximum hardness is reached, within the experimental error of hardness testing, before visible carbides disappear from the quenched microstructure and it is felt that the probable carbide content under such conditions is too small to produce the substantial decrease in hardenability from either lack of carbon solution or the nucleation effect, or both. Also, this effect was of importance only in S.A.E. 3240 and 4340, in both of which diffusion rates are notoriously slow. The diffusion concept can be used with equal facility to explain the increase in hardenability with quenching temperature increase from 1450 to 1525 degrees Fahr. (790 to 830 degrees Cent.) for these same two steels when quenched from a normalized prior structure. Here, as well, carbon solution is apparently complete at all quenching temperatures (Figs. 21 and 25).

The decrease in hardenability of all three rapidly cooled prior structures of S.A.E. 4340 with increase in time (Fig. 24) deserves some mention, particularly since the same tendency was noted in several of the analyses investigated. This is an apparent anomaly since all factors previously considered would tend to increase hardenability. The bars of S.A.E. 4340 used for this work possessed a substantial degree of heterogeneity in the form of banding. Parke and Herzig (9) have shown that if a hardenability criterion other than that of the penetration of maximum hardness is used, then

any reduction in the degree of gross heterogeneity should result in decreased hardenability. While segregation factors were not determined to check this point and no reduction in the visible degree of banding with increases in time could be observed microscopically, the authors feel that some such effect may be the cause of the condition observed. The same line of reasoning would explain the decrease in hardenability of the normalized prior structure of this analysis when quenched from the higher temperatures (Fig. 25). This concept of gross heterogeneity should not be confused with the microscopic diffusion of alloy carbide components discussed above.

No explanation can be given for the increase in hardenability of the normalized and quenched prior structures of S.A.E. 3240 at the short time periods (Fig. 20). From 10 minutes on, however, the effect is so small as to barely exceed the limit set for considering such changes as appreciable.

## Summary and Conclusions

1. In the carburizing S.A.E. 4620 type, time at temperature up to 10 minutes shows a discernible hardenability increase only from the two coarser initial structures. Times beyond this interval, as well as all periods on the faster cooled structures, had no significant effect. A temperature of 1450 degrees Fahr. (790 degrees Cent.) is unsuitable for developing full hardenability in this composition while temperatures in excess of 1500 degrees Fahr. (815 degrees Cent.) offer no advantage in obtaining better response to quenching.
2. Steels in the medium carbon range reacted essentially alike. The prior structures of all analyses divided themselves into two groups as affected by time at temperature and quenching temperature, i.e., spheroidized and annealed in one group and the hot-rolled, normalized, and quenched in the other.
3. The spheroidized and annealed prior structures were very sensitive to the heating intervals employed, yielding values far below normal expectancy at the shorter time periods. This range was less for the low alloyed NE 9442 grade, and was substantially greater for the higher alloyed types.
4. The rapidly cooled prior structures showed no important changes in hardenability over the time period studied with the exception of—

(a) the increase in hardenability at short time intervals of S.A.E. 3240 from the normalized and quenched prior structures, for which no logical reason could be advanced, and

(b) the significant decrease of the S.A.E. 4340 grade from all the more rapidly cooled prior structures when exposed for a 4-hour interval, which was attributed to partial homogenization of a banded structure.

5. Among the higher alloyed medium carbon steels, the normalized prior structures produced higher hardenability at all quenching temperatures investigated. With increasing quenching temperature, the normalized either quickly became constant or attained a maximum value and decreased slightly. The annealed prior structure showed a steady increase with quenching temperature. Above 1500 degrees Fahr. (815 degrees Cent.), both prior states were identical in the case of NE 9442.

6. Probably more than any other single factor in a given heat of steel, the exact size, shape and distribution of the carbides dictate the success or failure of quenching treatments utilizing heating cycles confined to short times at temperature.

7. From the results obtained on the higher alloyed medium carbon steels, it appears impossible to predict the hardness traverse of production parts treated from readily machinable prior structures unless the hardenability test is also conducted under reasonably equivalent conditions of time, temperature and prior structure.

8. From a hardenability standpoint, the advantages of long soaking times when conducted on these alloy steels from normalized, hot-rolled or quenched prior conditions appears to have been overestimated. In fact, some of the data contained herein show indications of loss of hardenability under these conditions.

9. The physical properties determined on S.A.E. 4140 and 4340 in through hardening test sections suggest a response to the variables considered which is parallel to, but of much less extent than, the hardenability variation.

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9. Parke and Herzig; *Metals and Alloys,* Feb. 1942, p. 241.

## DISCUSSION

**Written Discussion:** By Morse Hill, assistant metallurgist, Materials Laboratory, Engineering Division, Materiel Command, Army Air Forces, Wright Field, Dayton, Ohio.

The authors have added notably to the knowledge of the effects of variables on the hardenability of steels. It is to be regretted that their work was confined to but one heat of each type of steel, for, as shown by Williams and as reported by the writer last year, different heats behave differently with respect to time and temperature even with identical initial structure. For instance, heats of 4130 steels have been found, one of which, even though quenched from 1700 degrees Fahr. (925 degrees Cent.) showed no change in hardenability with increasing quenching temperature, while another showed a decided increase in hardenability for each 100 degrees increase in the quenching temperature. This increase was accompanied by no change in the grain size.

In this connection, have the authors any information on the as-quenched grain size of their specimens? It would seem that this as well as carbide solution is a possible cause of hardenability change. The grain size is conveniently measured by slotting the specimen with a water-cooled wheel about 1/16 from the quenched end about 0.25 inch deep and breaking off the piece thus formed with a press. Comparison may then be made with a set of Shepherd standards.

**Written Discussion:** By Gordon T. Williams, metallurgist, Pratt & Whitney Aircraft, E. Hartford, Conn. (Formerly metallurgist, Deere & Co., Moline, Ill.)

The data so effectively presented by the authors deserve consideration by all who heat treat alloy steels to specification; as confirmation and addition to the writer's earlier paper (ref. 6) it is of particular interest to him.

The results of the work reported in these two papers show how greatly hardenability is affected by prior structure and by time at heat. This leads to the important conclusion, not stressed by the authors, that use of the S.A.E. standard hardenability procedure may give results not in line with production heat treating results. The standard procedure specifies normalizing of steel before testing, and also stipulates that the test piece shall be held at heat for 20 minutes before end quenching.

Unless production heat treating cycle is similar in both these respects, the response to actual hardening may be very different from expectations based on "standard" hardenability results. Further, the difference cannot be predicted, since both individual heat and alloy type show variations in effect of prior structure and of time at hardening heat.

In other words, if a certain alloy steel is in actual use to be annealed to lamellar pearlite, then later hardened after one hour at heat, the hardenability found thus may be considerably (and unpredictably) different from the indication of a Jominy test carried out under S.A.E. standard conditions. The writer has found many confirmations of the above statement, particularly in observation of several hundred heats of one type of alloy steel used in production of an ordnance item. To obtain hardenability test results useful for predicting production results, it was found necessary to test the steel with the same prior structure it would have in production (in this instance a cycle anneal) and to hold the specimen at heat for the same length of time as the production part would encounter. If mill-annealed steel had been used, a variety of prior structures would have been encountered, and their important effect would have been obscured by use of the specified normalizing treatment.

The writer believes that the hardenability test to be most directly useful should be based on a thermal cycle the same as will be used in production. This unfortunately means that such tests will not be "standard," and the results hence not transferable, but such a conclusion is clearly to be drawn from the authors' data.

## Oral Discussion

GERALD D. RAHRER:[1] I have a question concerning the method of determining the grain size of the samples. Was McQuaid-Ehn or as-quenched grain size determined? If the latter, was a metallographic or the fracture method used?

F. M. WALTERS, JR.:[2] The authors would have been pleased with their results on the effect of quenching temperature if they had applied the necessary correction for the effect of quenching temperature on the cooling rates at various points along the end quenched part. Work by Jackson and Christenson[3] has shown that the higher the quenching temperature of the end quenched bar the slower the cooling rate, so that those steels which showed no effect of quenching temperature would have shown a slight increase in hardenability as the quenching temperature was raised, and those which the hardenability decreased slightly with quenching temperature would level off.

MORRIS BLUM:[4] I have found that normalizing prepared Jominy test pieces prior to heating for quenching resulted in considerable increased hardenability. Discounting the effect of lowering the coarsening temperature by normalizing thereby increasing hardenability, could this increase be explained? Test samples were from 30 carbon, high nickel, chromium, molybdenum steel and considerable banding can be expected. Could there be a homogenizing effect with this treatment? Test samples were taken at the pouring platform from the as-rolled slabs, and plates, the trend in hardenability being in the same direction after normalizing.

W. E. JOMINY:[5] This paper is of considerable interest to all of us who are

[1]Alloy Bureau, Metallurgical Division, Carnegie-Illinois Steel Corp., Chicago.

[2]Superintendent, Division of Physical Metallurgy, Naval Research Laboratory, Washington, D. C.

[3]Metals Technology, December 1943.

[4]Metallurgist, Carnegie-Illinois Steel Corp., Gary, Indiana.

[5]Metallurgist, Dodge Chicago Plant, Division of Chrysler Corp., Chicago.

interested in heat treatment. The time at temperature is exceedingly important since it affects the use of our equipment. Certainly, if we can get along with less than ten minutes at heat or if we are required to go to four hours at heat, it makes a big difference to us and is a matter of considerable commercial importance. I have been rather surprised to find the fact that four hours' heating does not seem to bring the steels together, in some cases, with different previous treatments. I do not know whether anyone expected that. Certainly I did not. I have been under the impression that the time at heat more or less is a matter of the size of the piece you are using though previous structure was also considered. Of course, if you define the time at heat as the time after the center of a piece gets to heat, then you wash out the effect of size of the piece you are using. But there seems to be a tendency that the larger the part the longer you hold at heat. Something that each of us has to decide is how long should a sample be heated before we quench it. It is very enlightening to find in some of these steels there is a very great difference in the effect of heating time on the hardenability. I wonder if the authors have done any work on the effect of time at heat on physical properties. I presume in the fully hardened part of the curve in all cases you get the same physical properties. I was just wondering whether the authors have anything to say about that.

It seems to me this subject affects us very greatly. It affects practically every heat treating specification we have because we have to tell those doing the work how long to hold the steel at heat before quenching it.

**Authors' Reply**

In answer to Mr. Hill's request for information regarding the effects of these variables from heat to heat of a given type of steel, may we say that we would like to have such information just as much as he. Lack of sufficient time and manpower have prevented us from doing more than has been reported here.

Both Mr. Hill and Mr. Rahrer have asked questions concerning the grain size of these steels. As stated in the paper, oxidation grain size information was obtained under all conditions of test from both normalized and annealed prior structures. No appreciable change in grain size could be ascertained, hence the statement that grain size was not considered as a factor in this investigation.

We are in agreement with Mr. Williams' remarks concerning the need for taking the effects of these variables into consideration in performing the hardenability test when correlation with production heat treating results is desired. It seems advisable, however, to have a so-called "standard" test upon which different laboratories can standardize and the present one involving a normalized prior structure and a constant time at temperature seems satisfactory. The user needs to remember that the results obtained by the standard test may not apply to his production conditions.

Dr. Walters is entirely correct in calling attention to the need for small cooling rate corrections in expressing the effect of quenching temperature by hardenability curves. It was felt, however, that since the ASTM hardenability chart is in general use regardless of quenching temperature, the results would be of more general practical use presented in this way.

We have not experienced any significant variation between hot-rolled and

normalized prior structures as reported by Mr. Blum but the conditions are sufficiently different to possibly account for the discrepancy. All of our work has been done on 1.25-inch diameter hot-rolled bars, whereas the physical heterogeneity existing in hot-rolled shapes may be sufficiently great to allow an improvement on normalizing. Our own work on as-cast versus normalized cast specimens would indicate no important difference in hardenability.

The authors were certainly as surprised as Mr. Jominy in finding such substantial effects of time and prior structure on some of the alloy steels studied. Many of the time at temperature intervals used in production treating of large sections could undoubtedly stand some re-examination in the light of these data. In addition, these results present a potent argument in favor of prior normalizing of large sections. The difference in time at temperature between the surface and center of a large section will produce a depth of hardness below expectations from an annealed prior structure unless exceedingly long heating times are used.

The authors wish to express their appreciation to the discussers of this paper.

# THE STRESS DISTRIBUTION AT THE NECK OF A TENSION SPECIMEN

By P. W. Bridgman

*Abstract*

*By approximating to the contour of a tension specimen at the neck by a circle and by using a circle to approximate the lines of principal stress in the neighborhood of the neck, the distribution of stress across the neck has been found which rigorously satisfies the conditions of plasticity in the conventional form of von Mises. The same solution also applies with an error of only a few per cent when strain hardening occurs of the amount found under actual conditions. The solution differs qualitatively from the stress distribution in an elastically strained specimen. In the plastic specimen, the tension is greatest on the axis and least on the periphery; the stress system consists of an axial tension, uniform all the way across the neck, plus a hydrostatic tension, which is zero on the periphery and increases to its maximum value on the axis.*

*The effect of the variation of tension across the section is to make the mean tension higher than the true tension of flow. Numerical values and curves are given for converting one tension to the other. Under extreme conditions recently attained experimentally, the correction may amount to 40 per cent. The correction depends on a single parameter, $a/R$, the ratio of the radius of the neck to the radius of curvature of the contour of the neck. Under experimental conditions $a/R$ is determined to a certain degree of approximation by the reduction of area only, so that the correction may be roughly applied given the reduction of area only.*

*There appears to be a close connection between the "cup and cone" fracture often observed and the stress distribution at the neck. The brittle fracture on the axis is associated with the hydrostatic tension prevailing there, while the shearing fracture nearer the outer surface is connected with the shearing stresses which become important near the outer surface.*

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A paper presented before the Twenty-fifth Annual Convention of the Society, held in Chicago, October 18 to 22, 1943. The author, P. W. Bridgman, is associated with the Physics Department, Harvard University, Cambridge, Mass. Manuscript received June 10, 1943.

THE stress-strain curve which is deduced from the ordinary tension test is properly a curve of average stress against average strain at the neck. It is almost certain, however, that the stress is not constant across the neck, and the question arises as to whether the variation is extensive enough to alter materially any deductions that we make from the behavior of the averages, in particular our deductions about strain hardening. A rigorous solution of the problem in plastic flow involved here does not seem possible at the present time. Apparently the only approximate solution is that of Siebel,[1] and this involves several doubtful simplifications, which will be referred to again later.

One might perhaps hope to get some hint as to a plausible order of magnitude for the variation of stress across the neck from the solution of the corresponding elastic problem. The elastic distortion in the immediate neighborhood of the neck must be roughly like the solution worked out rigorously by Neuber[2] for a hyperboloid of revolution. One may draw the conclusion from this known solution that probably if the reduction of area is only 50 or 60 per cent, which is of the order of magnitude of the reduction at fracture of ordinary ductile steels, the effect of lack of uniformity of stress distribution is not important. Recently, however, I have found[3] that by conducting the tensile test in a fluid at pressures of the order of 400,000 lb/in$^2$ reductions in area up to nearly 100 per cent may be realized without fracture, and strain hardenings, calculated on the basis of the average stress, may be realized up to a factor of 3 or more. Under these conditions the contour of the specimen at the neck may have such a small radius of curvature that the elastic solution indicates variations of stress across the section of several hundred per cent, and it obviously becomes important to make an approximate estimate of the departures from uniformity of the stresses in actual cases of plastic flow.

A complete solution should be capable of giving, among other things, the shape of the external contour of the tension sample. In fact, one might anticipate that one of the uses that could be made of a complete solution would be to provide quick information about the strain hardening curve from the shape of the contour. This, however, seems impossible at present. The best that I have been

[1] E. Siebel, Berichte der Fachauschüsse des Vereins deutscher Eisenhüttenleute, Werkstoffausschuss, Bericht Nr. 71, Nov. 5, 1925.

[2] H. Neuber, Beiträge für den achssymmetrischen Spannungszustand; Thesis, München, 1932.

[3] P. W. Bridgman, American Scientist, 31, 1, 1943.

able to do in the solution given in the appendix is to assume the external contour given, and to deduce a set of stresses that satisfies the conditions of plasticity in the immediate neighborhood of the neck.

The factor $\left(1 + 2\frac{R}{a}\right) \log \left(1 + \frac{1}{2}\frac{a}{R}\right)$ and certain other related data are given in Table I. The inverse of the factor, which may be called simply the "correction factor," since it is the factor by which the "uncorrected true stress" is to be multiplied to obtain the "corrected true stress" is shown as a curve against a/R in Fig. 1 The "corrected true stresses" given by the present analysis are progressively larger than the "corrected true stresses" that would be given by Siebel's formula.

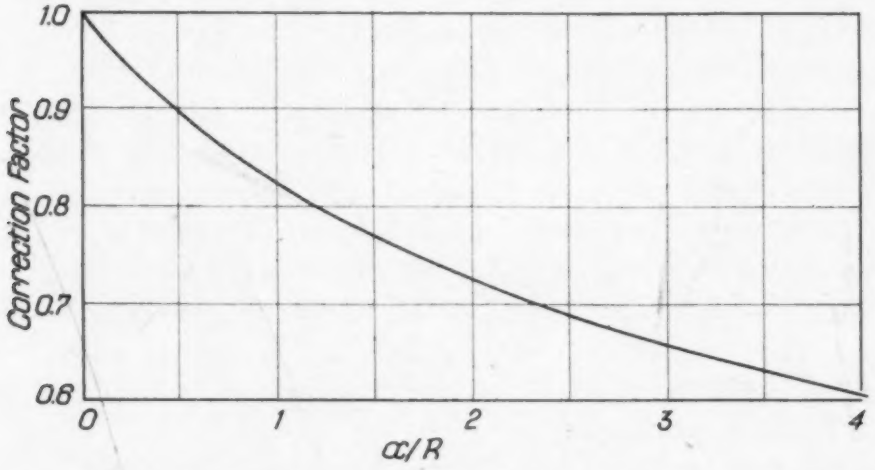


Fig. 1—The Correction Factor as a Function of Radius of Curvature of the Contour of the Neck.

Table I

| $\frac{a}{R}$ | Inverse Correction Factor, $\left(1 + 2\frac{R}{a}\right) \log \left(1 + \frac{1}{2}\frac{a}{R}\right)$ | Siebel's Factor $1 + \frac{1}{4}\frac{a}{R}$ | $\frac{\widehat{rr}_0}{F}$ | $\frac{\widehat{rr}_{aver}}{F}$ |
|---|---|---|---|---|
| 0 | 1 | 1 | 0 | 0 |
| 1/8 | 1.078 | 1.083 | .154 | .078 |
| 1/4 | 1.115 | 1.125 | .223 | .115 |
| 1 | 1.215 | 1.250 | .405 | .215 |
| 2 | 1.386 | 1.500 | .693 | .386 |
| 3 | 1.524 | 1.750 | .916 | .524 |
| 4 | 1.649 | 2.000 | 1.099 | .649 |

The corrections are quite appreciable even under ordinary conditions of testing. Thus for a steel of approximately 0.45 carbon content a representative reduction of area at fracture is 60 per cent, and at this reduction a representative value of a/R is 0.8. (a is

the radius of the cross section and R is the radius of curvature of the longitudinal surface fibers, at the cross section of least diameter.) Under these conditions F (the "flow stress," or stress required for flow in simple tension) is 15 per cent lower than $zz_{aver}$ (the average longitudinal tension), and therefore the strain hardening, calculated without making the correction, 17.6 per cent too high. Under greater strains, such as may be produced by pulling under hydrostatic pressure, the correction may change even the sign of certain terms and thus change the qualitative aspect of the picture. The change will be greatest with respect to fracture. It appears that the fracture is essentially determined by the hydrostatic tension on the axis, and this tension is large enough numerically, even in ordinary cases, to demand that it be given as well as the longitudinal tension in specifying the conditions of fracture in an ordinary tensile test. This matter is elaborated further in one of the symposia of this meeting. One important result remains, however, even after the correction is applied. After the first initial stages of a tension test, it is coming to be recognized that the stress-strain curve is linear in the natural strain, that is, the "uncorrected true stress" gives a linear plot against $\log_e A_0/A$, $A_0$ and A being the initial and final neck areas. Experiments indicate that over a range of conditions "corrected true stress" is also linear. The subject requires further study, but at least I have found no cases in which the corrected curve was not also linear within experimental error.

In practise, in order to apply the correction, the radius of curvature at the neck must be measured in addition to the other data which it is now conventional to collect. This may be done by various devices, but it would be more convenient if it should prove that a/R is a function only of the reduction of area. There are present indications that any departures of a/R from being a function of reduction of area only may be by amounts unimportant for purposes of the correction. The matter demands extensive study over a wide range of conditions, but in the meantime a curve is shown in Fig. 2 representing the average results of some 50 experiments on a variety of steels. Most of these were on a 1045 steel, heat treatments varying from annealed to quenched and drawn at 800 degrees Fahr., but also included a dead soft 1020 steel, a silicon-manganese alloy steel treated to a strength of around 300,000 lb/in$^2$ and a tough nickel steel. At a value of $\log_e A_0/A$ of 3.0 the extreme variation

found in a/R was from 1.3 to 2.0. There seems no correlation between the composition of the steel and departure of a/R from the median curve. Even brass and a bearing bronze were found to fall in the same limits as the steels. In the extreme case the correction factor computed from the directly measured a/R does not differ by more than 4 per cent from the factor from the median curve. There are factors yet to be investigated. For instance, does the ratio of

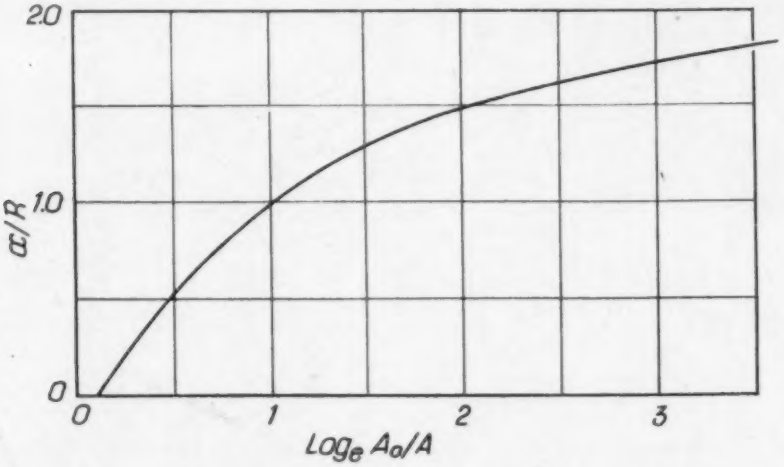


Fig. 2—Average Contour Factor $\left(\frac{a}{R}\right)$ from a Number of Experiments as a Function of the "Natural Strain" at the Neck.

length to diameter of the original specimen affect the values of a/R? All the measurements referred to above were made with a value for this ratio in the neighborhood of 3. However, in the absence of direct measurements of a/R the corrected value of "true stress" obtained by assuming the a/R of Fig. 2 is doubtless better than the "uncorrected true stress." To assist in making the reduction, Figs. 1 and 2 have been combined to give Fig. 3, in which the correction factor is plotted against $\log_e A_0/A$. This curve is to be used only subject to the precautions suggested by the discussion.

The solution has assumed that the hardening is constant all the way across the neck, that is, it has assumed that the hardening is not affected by the hydrostatic tension that acts in addition to the stress $\widehat{zz}_a$ at the boundary. The two last columns of the Table show the ratio of the maximum (on the axis) and the average hydrostatic tension to the $\widehat{zz}$ component of stress at the edge. Consider a typical example in which F = 355,000 pounds per square inch for a natural strain of 2, at which a/R is approximately 1.5. $\widehat{rr}_0/F$ is approximately 0.55, which means a hydrostatic tension on the axis

of approximately 196,000 pounds per square inch, and an average hydrostatic tension over the section of 106,000 pounds per square inch. Now I have found by experiment that the flow stress when necking begins is increased from 10 to 15 per cent by a hydrostatic *pressure* of 355,000 pounds per square inch. This means that under the condition in our example the flow stress would be decreased by

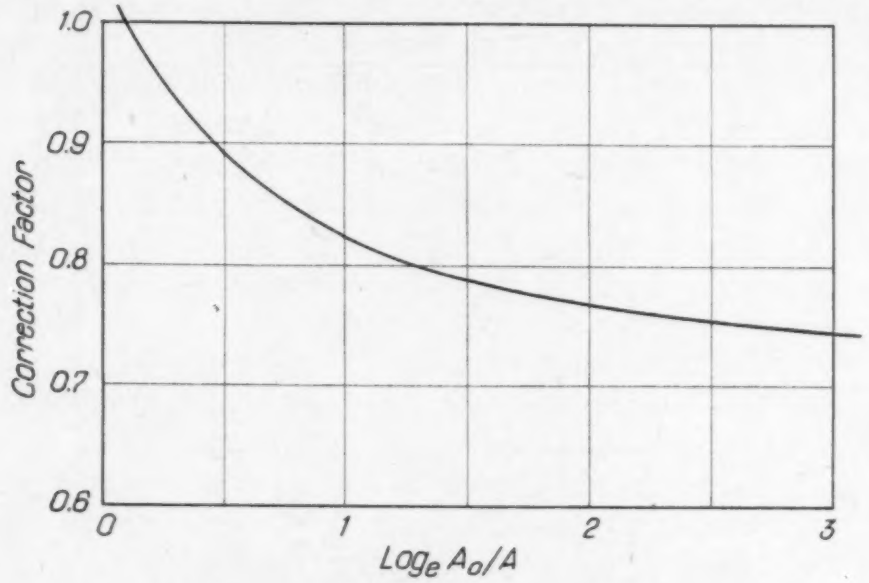


Fig. 3—Correction Factor for Reducing Average Tensile Stress to "Flow Stress," as a Function of Natural Strain at the Neck, Assuming a Mean Experimental Connection Between the Shape of the Contour of the Neck and Reduction of Area.

some 3.8 per cent by the hydrostatic tension prevailing across the neck. This correction is in the opposite direction from that already applied; it is so small that perhaps it may be neglected in comparison with other uncertainties.

The total tension on the axis differs from that at the outer edge by $\widehat{rr}_0$ (the radial tension on the axis), that is, the ratio of the axial to the peripheral tension is $1 + \widehat{rr}_0/F$. In Fig. 4 this is plotted against $\log_e A_0/A$, assuming the same empirical relation between $a/R$ and $\log_e A_0/A$ that was used in constructing Fig. 3. The practical use of the figure is therefore subject to the same precautions as use of Fig. 3. This curve will be of service in computing the fracture stress, since as will appear in the discussion presently, fracture is doubtless initiated on the axis.

Finally, we consider certain applications that may be made of our solution to the problem of the nature of the fracture. The maximum shearing stress at the neck, assuming the solution given,

is constant across the neck, has the value $\widehat{zz}_a/2$, and is equal on the r − z and r − $\theta$ planes. That is, at every point there is a cone of shear. The shearing stress in the r − $\theta$ plane vanishes. Because of the geometrical limitations any actual slip of the material must probably be on the r − z planes. The greatest shearing stress,

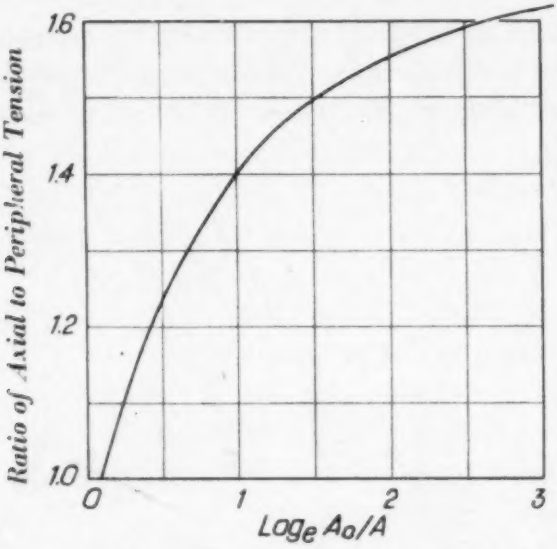


Fig. 4—The Ratio of the Tensile Stress ($\widehat{zz}$) on the Axis to its Value at the Periphery, as a Function of the Natural Strain at the Neck, Assuming the Experimental Connection Between Contour Shape and Strain Shown in Fig. 2.

however, is not at the neck. Referring to Fig. 5 of the appendix, and recalling the boundary conditions, at the point P there is a shearing stress along the plane bisecting AB and CD of $\widehat{zz}/2 \cos^2 \alpha$, and along the plane cutting the plane of the paper in CD at an angle of 45 degrees of $\frac{1}{2}$ [$\widehat{zz}/\cos^2 \alpha - \widehat{\theta\theta}$]. The sign of $\widehat{\theta\theta}$ at points on the boundary not on the neck would seem to be in some doubt, so that it is not at once obvious which of these two shearing stresses is the larger. Geometrical limitations, however, would seem to demand that actual slip of the material take place in the first plane, bisecting AB and CD. This agrees with observation; slip on the other plane takes place less commonly, and even then usually only when slip can spread right across the neck to a symmetrical point on the other side.

The shearing stress $\widehat{zz}/2 \cos^2 \alpha$ is composed of two factors, the first of which, $\widehat{zz}$, decreases on receding from the neck, and the second of which, $1/\cos^2 \alpha$, at first increases. The variation of $\widehat{zz}$ is not fixed by the analysis above, only the average $\widehat{zz}$. If the neck is

abrupt, $1/\cos^2 \alpha$ increases so rapidly in the neighborhood of the neck that it swamps the decrease of $zz_{aver}$, and also any plausible decrease of the actual $\widehat{zz}$. Observation of many tensile fractures in necked samples shows that at the outside failure is frequently along a shear plane, and this shear never issues at the neck itself, but a little removed from it. To give a numerical example, the specimen for which a/R was 2 at a reduction in diameter to one quarter had a maximum $zz/\cos^2 \alpha$, assuming $\widehat{zz}$ uniform across every section, 14 per cent greater than at the neck. The point of maximum was

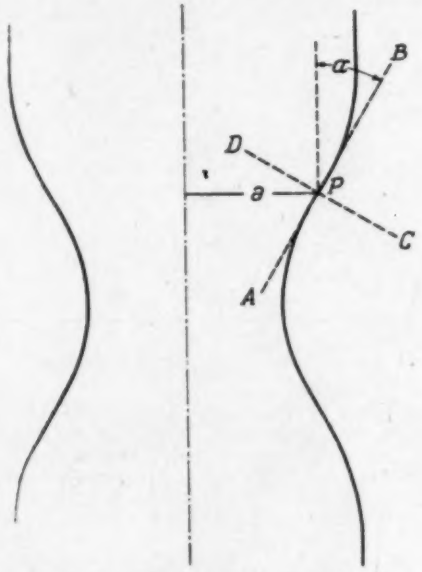


Fig. 5—Certain Geometrical Relations Used in the Analysis (p. 562).

displaced along the axis from the neck by about 0.4 of the neck diameter. With regard to the assumption of uniformity of $\widehat{zz}$ it is probable that as one proceeds away from the neck toward the elastic region $\widehat{zz}$ will tend to assume the property of the elastic solution, that is, to have the greatest value at the outside surface instead of on the axis as in the full plastic region at the neck. The effect of this direction of variation in the lack of uniformity of $\bar{z}z$ will accentuate the tendency of the shearing stress to have its maximum value away from the neck.

The conclusion that at the neck the tension is greatest on the axis and least at the outside, instead of inversely as in the elastic case, has interesting reactions on our picture of the mechanism of fracture. We have seen that the stress on the axis may be regarded as differing from that at the edge, where it is a simple tension, merely

by the addition of a hydrostatic tension. This superposed hydrostatic tension will have two effects. In the first place there will be a reduction in the tension component in excess of the hydrostatic stress required to produce fracture. It is true that this has not been established by direct experiment, but it has been established for the grades of steel that permit necking that the excess tension component at fracture is increased by hydrostatic pressure, and since these effects are usually linear, we may expect a decrease with hydrostatic tension. In the second place, it is known that hydrostatic pressure increases ductility, so that a hydrostatic tension may be expected to decrease it. It may be that these two effects are not completely independent of each other, but in any event they are both in the same direction, and conspire to produce the brittle tensile fracture at the axis which is usually shown by the grades of steel that exhibit necking. Although there has in the past been difference of opinion, it seems to be becoming accepted now that the fracture of a necked specimen starts on the axis. This is shown convincingly, for example, by a photograph on page 55 of Gensamer's Strength of Metals under Combined Stresses.

Our solution demands that the tendency to brittle fracture diminishes as one recedes from the axis. On the other hand, the tendency to shearing slip increases at distances from the axis. On the axis the geometrical conditions are unfavorable because slip will have to occur on curved conical surfaces, whereas toward the outside the slip occurs more nearly on planes. Another important feature in the geometrical situation is that shearing fracture cannot get initiated unless there is freedom of slip all the way across the slip planes; slip cannot start if one end of the slip planes is anchored on the axis, whereas a tensile break spreading from the axis provides a possible point of initiation for shearing slip. It is the balance between the two tendencies to tensile and shearing fracture that gives the ordinary "cup and cone" fracture.

This view would demand that the fracture of a necked test piece begin on the axis as a tensile break, where the tendency to tensile fracture is the greatest, and also that the tensile break be situated at the narrowest part of the neck. This latter agrees with observation; longitudinal sections made through a number of "cup and cone" breaks shows that the flat bottom of the cup is always located at the narrowest part of the neck. The tensile fracture travels toward the outside until the geometry is so modified that the shear-

ing fracture can take over. Precisely what the critical condition is that determines when shear is ready to take over is a subject for future investigation.

If the pulling is done in a medium under hydrostatic pressure the general ductility increases, the tendency to brittle tensile fracture diminishes, and the shearing type of fracture will become more prominent. This agrees with recent observations, as yet unpublished, that above a certain pressure the fracture becomes almost, if not entirely, shearing in character.

## *Appendix*

### *Summary of Principal Symbols Used.*

The stress system is referred to conventional cylindrical co-ordinates, r, $\theta$, and z, and the notation for the stress components is that adopted, for example, in Love's Mathematical Theory of Elasticity. In particular, the stress components are: $\widehat{rr}$, $\widehat{\theta\theta}$, $\widehat{zz}$, $\widehat{\theta z}$, $\widehat{zr}$, and $r\theta$. Other symbols are:

a, outside radius of the cross section at the neck.

R, radius of curvature at the neck, of the section through the neck containing the axis

F, "flow stress," tension at which plastic flow occurs, the two other principal stress components being zero.

$A_0$, initial cross section of the tension sample.

A, final section at the neck of the tension sample.

### *Derivation.*

Certain necessary conditions are imposed on any solution by the stress equations of equilibrium. The problem may be assumed to have rotational symmetry about the axis. Using ordinary cylindrical co-ordinates, this means that all derivatives with respect to $\theta$ vanish, and the $\widehat{r\theta}$ and $\widehat{\theta z}$ stress components vanish identically. The usual three stress equations of equilibrium reduce to two:

$$\left.\begin{aligned} \frac{\partial \widehat{rr}}{\partial r} + \frac{\partial \widehat{rz}}{\partial z} + \frac{\widehat{rr} - \widehat{\theta\theta}}{r} &= 0 \\ \frac{\partial \widehat{rz}}{\partial r} + \frac{\partial \widehat{zz}}{\partial z} + \frac{\widehat{rz}}{r} &= 0 \end{aligned}\right\} \qquad (1)$$

The external curved surface is free from stress, and the boundary conditions become:

$$\left.\begin{aligned} \widehat{rr}\cos\alpha - \widehat{rz}\sin\alpha &= 0 \\ \widehat{rz}\cos\alpha - \widehat{zz}\sin\alpha &= 0 \end{aligned}\right\} \text{at external surface.} \qquad (2)$$

Here $\alpha$ is the angle between the generating line of the external surface and the axis, as indicated in Fig. 5. The conditions at the surface may be rewritten as:

$$\left.\begin{aligned} \widehat{rr} &= \widehat{zz}\tan^2\alpha \\ \widehat{rz} &= \widehat{zz}\tan\alpha \end{aligned}\right\} \text{ at external surface.} \tag{3}$$

At the external surface the planes of principal stress are: (1) the plane of the axis (plane of the paper in Fig. 5) across which the normal stress is $\widehat{\theta\theta}$, (2) the tangent plane (perpendicular to the plane of the paper and with trace AB in Fig. 5) across which the normal stress is zero, and (3) the plane perpendicular to (1) and (2) (trace CD in Fig. 5) across which the normal stress is $\widehat{zz}/\cos^2\alpha$.

At any section perpendicular to the axis,

$$2\pi\int_0^a r\,\widehat{zz}\,dr = \text{Load} = \text{constant} \tag{4}$$

The conditions simplify at the neck. It is assumed that the specimen is symmetrical on both sides of the neck. Hence at the neck:

$$\left.\begin{aligned} \frac{\partial\widehat{zz}}{\partial z} &= 0 \quad \text{for all } r \\ \widehat{rz} &= 0 \quad \text{for all } r \\ \widehat{rr}_a &= 0 \\ \widehat{rr}_0 &= \widehat{\theta\theta}_0 \end{aligned}\right\} \text{ at the neck.} \tag{5}$$

also

A stress symbol with subscript "a" denotes the value at the external boundary, subscript 0 at the axis. The first two conditions of (5) arise from symmetry. The third expresses the freedom of the external surface from stress. The last of the four conditions, which also holds at all points on the axis, is necessary in order to avoid infinities in the first of equations (1).

Let us now inquire what is a plausible solution at the neck for $\widehat{rr}$, $\widehat{\theta\theta}$, and $\widehat{zz}$, $\widehat{rz}$ not being considered. If $\widehat{rz}$ is eliminated between the two stress equations, a single equation results for the three stresses:

$$\frac{\partial}{\partial r}(r\cdot\widehat{rr}) = \widehat{\theta\theta} + \int_0^r r\,\frac{\partial^2\widehat{zz}}{\partial z^2}\,dr \tag{6}$$

If we put

$$\widehat{zz} = f_1(r) + \tfrac{1}{2}z^2 f_2(r), \tag{7}$$

where $f_2(r) \equiv \dfrac{\partial^2\widehat{zz}}{\partial z^2}$, $f_1$ and $f_2$ are subject only to the restrictions:

$$2\pi\int_0^a f_1(r)\,r\,dr = \text{Load} \tag{8}$$

and

$$\frac{a}{R}\,\widehat{zz}_a = -\int_0^a f_2(r)\,r\,dr, \tag{9}$$

where R is the radius of curvature of the contour at the neck and a is now the radius of the neck. Equation (9) comes from applying condition (4) to a plane section just above the neck.

Subject to these conditions, a great deal of latitude is possible in the solution; in fact, having assumed $f_1$ and $f_2$ subject to restrictions (8) and (9), one may assume any $\widehat{rr}$ subject only to the condition $\widehat{rr}_a = 0$, and then solve (6) for $\widehat{\theta\theta}$. The problem is to pick out from this infinity of solutions those which satisfy the plasticity conditions.

We first proceed on the assumption of no strain hardening. The plasticity conditions are now of two sorts. First there is the condition that the material be in the plastic condition all the way across the neck. We assume the form of von Mises:

$$(\widehat{rr} - \widehat{\theta\theta})^2 + (\widehat{\theta\theta} - \widehat{zz})^2 + (\widehat{zz} - \widehat{rr})^2 = \text{constant, independent of r at the neck.} \tag{10}$$

Second, there are the flow conditions, written in the accepted form in terms of the strain velocities:

$$\left.\begin{aligned} \dot{e}_r &= \beta[\widehat{rr} - \tfrac{1}{2}(\widehat{\theta\theta} + \widehat{zz})] \\ \dot{e}_\theta &= \beta[\widehat{\theta\theta} - \tfrac{1}{2}(\widehat{zz} + \widehat{rr})] \\ \dot{e}_z &= \beta[\widehat{zz} - \tfrac{1}{2}(\widehat{rr} + \widehat{\theta\theta})] \end{aligned}\right\} \tag{11}$$

In the general case the coefficient $\beta$ of these equations is neither a material constant nor a function of the physical parameters such as the stresses. It is rather a freely disposable function of the co-ordinates and varies from problem to problem with the geometry. The equations merely express the isotropy of flow at any single point.

If it is not possible to find a set of stresses satisfying all the conditions one may draw the conclusion that the state of affairs at the neck is of necessity non-isotropic. Conversely, if a solution is possible, then an isotropic state of affairs at the neck is at least not ruled out.

Since the plasticity equations hold across the neck, we may particularize by writing them for an external point and for a point on the axis. Remembering that $\widehat{rr}_a = 0$, and $\widehat{rr}_0 = \widehat{\theta\theta}_0$, these become:

$$2\widehat{\theta\theta}_a^2 + 2\widehat{zz}_a^2 - 2\widehat{\theta\theta}_a\widehat{zz}_a = 2\widehat{\theta\theta}_0^2 + 2\widehat{zz}_0^2 - 4\widehat{\theta\theta}_0\widehat{zz}_0 \tag{12}$$

$$\left.\begin{aligned} \dot{e}_{r_a} &= \beta[-\tfrac{1}{2}(\widehat{\theta\theta}_a + \widehat{zz}_a)]; & \dot{e}_{r_0} &= \beta[-\tfrac{1}{2}\widehat{zz}_0 + \tfrac{1}{2}\widehat{\theta\theta}_0] \\ \dot{e}_{\theta_a} &= \beta[\widehat{\theta\theta}_a - \tfrac{1}{2}\widehat{zz}_a]; & \dot{e}_{\theta_0} &= \beta[-\tfrac{1}{2}\widehat{zz}_0 + \tfrac{1}{2}\widehat{\theta\theta}_0] \\ \dot{e}_{z_a} &= \beta[\widehat{zz}_a - \tfrac{1}{2}\widehat{\theta\theta}_a]; & \dot{e}_{z_0} &= \beta[\widehat{zz}_0 - \widehat{\theta\theta}_0] \end{aligned}\right\} \tag{13}$$

The condition of isotropy of flow is automatically satisfied on the axis, but elsewhere special adjustment will be necessary to meet both the flow conditions and the plasticity condition of von Mises.

Before proceeding further it will pay to look at the numerical values, to see whether we are concerned only with departures from

linearity which may be treated as small, or whether they are of a larger order of magnitude. If the tensile specimen is pulled to a reduction of area of about 94 per cent, it has been observed in the case of one experiment that a/R at the neck is approximately 2. Reductions up to nearly 100 per cent have been observed, so that values of a/R in excess of 2 are to be expected. If we assume $\partial^2 \widehat{zz}/\partial z^2 = \text{const}$, then the stress equation (6) becomes

$$\frac{\partial}{\partial r}(r \cdot \widehat{rr}) = \widehat{\theta\theta} - \frac{a}{R}\widehat{zz}_a \frac{r^2}{a^2} \tag{14}$$

For the sake of example put $a/R = 2$, and write the equation for the outer edge:

$$\frac{\partial}{\partial r}(r \cdot \widehat{rr})\Big|_{r=a} = \widehat{\theta\theta}_a - 2\widehat{zz}_a \tag{15}$$

It would appear then that in general $\widehat{\theta\theta}$ and $\widehat{rr}$ must be of the same order of magnitude as $\widehat{zz}$ and that we cannot hope to get an approximate solution of the flow and plasticity conditions by treating $\widehat{\theta\theta}$ and $\widehat{rr}$ as small compared with $\widehat{zz}$.

In searching for a qualitatively satisfactory solution it is natural to start with the solution for the elastically strained body worked out by Neuber for the case of a solid of revolution whose outer surface is a hyperbola. We may take this as approximating our problem in the neighborhood of the neck. In the elastic solution $\widehat{zz}$ is not uniform at the neck but has its smallest value at the axis and then rises continually, at first slowly, and then more abruptly toward the outer surface, where it reaches its maximum value. The total extent of the rise and the abruptness of the upturn both increase as a/R increases. For values of a/R between 0 and 2 the maximum value of $\widehat{zz}$ differs from the average $\widehat{zz}$ by approximately the fraction $\frac{1}{4}a/R$. On the axis, $\widehat{\theta\theta}$ and $\widehat{rr}$ are both positive, that is, of the same sign as $\widehat{zz}$. At first $\widehat{rr}$ and $\widehat{\theta\theta}$ both increase on leaving the axis; $\widehat{rr}$ presently passes through a maximum and plunges to the value zero at the outer surface with an abruptness increasing with a/R. $\widehat{\theta\theta}$ rises continually toward the outer edge with an abruptness the greater the greater a/R. In the range from 0 to 2 for a/R, $\widehat{\theta\theta}$ at the outer edge is roughly $\frac{1}{3}(a/R)\widehat{zz}_{aver.}$

If one tries to find a solution of the stress equations of equilibrium (1), which of course must always be rigorously satisfied, which has the qualitative aspects of the elastic solution, one will find that the plasticity and flow conditions cannot be satisfied. Some experimenting with simple algebraic forms that have the requisite rough qualitative behavior, combined with a study of the

demands expressed in equations (12) and (13), will, I think, convince one of this. Furthermore, since the $\widehat{rr}$'s and $\widehat{\theta\theta}$'s are of the same order of magnitude as $\widehat{zz}$, the failure of the elastic solution to meet the plasticity conditions is by a large amount. Large failures of isotropy are necessary if the stresses are to have the same qualitative configuration as in the elastic case. But the isotropic conditions can be maintained by a change in the qualitative picture. The isotropy of flow at the outside demands, according to (13) that $\widehat{\theta\theta}_a = 0$. But already $\widehat{rr}_a = 0$, and in all cases $\widehat{rr}_0 = \widehat{\theta\theta}_0$. It suggests itself therefore to try setting $\widehat{rr} = \widehat{\theta\theta}$ for all values of r. This automatically ensures the isotropy of flow at all points of the neck. If we put $\widehat{\theta\theta} = \widehat{rr}$ in the equations of equilibrium in the form (6) and integrate, we get:

$$\widehat{rr} = -\int_r^a \left\{\frac{1}{r}\int_0^r r\,\frac{\partial^2 \widehat{zz}}{\partial z^2}\,dr\right\} dr \tag{16}$$

We are free to assume any form for $\partial^2 \widehat{zz}/\partial z^2$ subject only to the restriction (9). Equation (16) shows that for any ordinary smooth variation of $\partial^2 zz/\partial z^2$ with r, $\widehat{rr}_0$ is going to be positive, and there is a two dimensional hydrostatic *tension* on the axis, as in the elastic case.

Inspection now shows that the von Mises plasticity condition is satisfied for all values of r if we set

$$\widehat{zz} = \widehat{zz}_a + \widehat{rr} \tag{17}$$

We are free to do this because $\widehat{zz}_a$ is not yet fixed, and $\widehat{zz}$ is subject to the single condition $2\pi\int_0^a (\widehat{zz}_a + \widehat{rr})rdr = \text{Load}$.

It is to be remarked that under these special conditions the von Mises plasticity condition becomes identical with the maximum shearing stress condition.

The stress system which we have just found consists of a uniform tension $\widehat{zz}_a$ in the z direction all the way across the neck, plus a superposed hydrostatic tension (three equal tensions along three mutually perpendicular directions) increasing from zero at the outside surface to $\widehat{rr}_0$ on the axis.

A complete solution requires that the coefficient $\beta$ of the flow equations be determined. This is to be so determined that, given the stresses, the components of flow satisfy the conditions imposed by the geometry. In general, when there is radial symmetry and the elongation along the axis, $e_a$, is constant, the radial displacement $\rho$ must satisfy the condition:

$$\rho = -\frac{e_a}{2}r + \frac{c}{r} \tag{18}$$

In this particular situation, because the material occupies the axis and infinities must therefore be avoided on the axis, $c = 0$, $\rho = -\frac{e_z}{2} r$, and $e_r = e_\theta = -\frac{1}{2} e_z$. That is, the strains are uniform all the way across the neck, and this holds independent of time. The flow equations must therefore also demand a uniform flow, and the coefficient $\beta$ of equations (11) is in this particular case a constant all the way across. At any instant of time the equations for the strains $e_r$, $e_\theta$, and $e_z$ have the same appearance as the flow equations. That is, the dots may be removed from the left hand side of equations (11). The coefficient $\beta$ may still be a function of time, but its precise value is of no particular interest to us.

How must this solution be modified when strain hardening is considered? The question is not academic, because we have seen that it is possible to increase the average flow stress by a factor of at least two or three under extreme but realizable conditions of necking. Furthermore, the phenomenon of necking is itself a strain hardening phenomenon and only occurs when the slope of the strain hardening curve decreases below a critical value.

In general the whole mathematical set-up must be modified when there is strain hardening. The general case may be very complicated; we simplify by assuming the strain hardening to be isotropic. Under these conditions equations of the same formal appearance as (11) remain, but these are now equations on the strains and not on the strain velocities, and represent the strains reached asymptotically in time under constant stress. The coefficient $\beta$ now becomes determinate in terms of material constants and such physical parameters as the stresses or strains. The coefficient $\beta$ must be consistent with experimental stress-strain curves for all particular and possible stress systems. How, or whether, $\beta$ can be uniquely determined from a single type of stress-strain curve, as, for example, simple tension, need not be discussed here. It is obvious, however, since $\beta$ has now become deprived of its role as a disposable function, that it is no longer possible to satisfy all the conditions of equilibrium etc. if there is an independent plasticity condition analogous to (10) still to be satisfied. Any equation of the type of (10) which persists in the strain hardening case must play the role of a mathematical identity expressing conditions already inherent in the three equations for the three principal strains. Under such conditions the right hand side of (10) now

becomes a variable, a function perhaps of the strains, determined so as to be consistent with experiment.

In the special case where the strains are uniform the whole picture very much simplifies. The solution we have just found, assuming no strain hardening, continues to apply to the strain hardening case if we are at liberty to assume that at every stage of the necking process the $\beta$ of equations (11) is constant all the way across the neck and that the right hand side of equation (10) is similarly constant all the way across. In the solution we have found the strains are constant all the way across, and the stress system is a tension constant all the way across with a variable superposed hydrostatic tension. If the superposed hydrostatic tension has no effect on the strain hardening, the physical conditions would be met and we could take over our simple solution. Now it is known that to a first approximation such is indeed the case; numerical values have been given in the body of the text indicating how good an approximation may be expected. We shall assume in the following that our solution applies also to the strain hardening case, with an appropriate change in the meaning of the right hand side of (10).

It is possible, therefore, to meet all the conditions, assuming isotropy of flow across the neck, with the qualitative difference compared with the elastic case that $\widehat{zz}$ increases toward the axis instead of decreasing. Such an increase would demand only a very small excess yielding of the material near the surface and furthermore meets certain qualitative demands imposed by the nature of the fracture, as will appear later. It therefore is not unplausible. The steps by which this stress system is set up are doubtless somewhat as follows. Yield starts at the outside surface, where the tensile stress in the elastic condition is a maximum. A very slight amount of plastic flow is sufficient to redistribute the stress approximately uniformly. The plastic condition works its way toward the axis; as the material in the neighborhood of the axis assumes the plastic condition the two dimensional hydrostatic tension ($\widehat{rr}_0 = \widehat{\theta\theta}_0 =$ positive quantity) remaining from the previous elastic condition produces extensional creep along the axis and so an additional component of tension along the axis.

We still have to find an explicit solution; with the formulation above this will depend on finding the proper expression for $\partial^2\widehat{zz}/\partial z^2$, which is still at our disposal. No direct method for obtaining the proper expression presents itself; another method will therefore be

adopted for obtaining a differential equation for the stresses at the neck. Fig. 6 represents the state of affairs in a neighborhood close enough to the neck to permit the external contour to be represented by a circle. The radius of the neck, a, and the radius of curvature, R, of the contour at the neck, are given. At the external surface we have seen that one of the lines of principal stress is normal to the

Fig. 6—The Geometrical Analysis Used in the Approximate Solution in the Neighborhood of the Neck.

surface, and we know that on the axis the lines are normal to the axis. We assume that in the immediate neighborhood of the neck the complete line of principal stress is a circle, with center on the axis. Consider the particular stress circle that cuts the contour at such a point as to subtend the small angle $\varphi$ at the center of curvature of the contour. The radius of curvature, R′, of the stress circle, is $a/\varphi$. Consider now a point at the neck distant r from the axis. Let the length r subtend an angle $\varphi'$ at the center of the circle R′.

Then $\varphi' = \frac{r}{a}\varphi$. Through the point r, perpendicular to the radius, there passes one member of the family of lines of principal stress of which the external contour is another member. This line is perpendicular to the radius r and the circle of radius R′. We may assume that this line is also a circle, and we might compute its radius. It happens, however, that to the order of small quantities in which we are interested this refinement is not necessary, and it will be sufficient to treat this line of principal stress as a straight line perpendicular to the radius at r. Consider now the element of volume bounded by two axial planes including between them the small angle $\theta$, by the cylinders with radii r and r + dr, by the plane perpendicular to the axis at the neck, and by the spherical surface of radius R′. By construction the forces across the faces of this element are entirely normal and are given by the principal stress components. The condition that the net component of force in the r direction on the six faces of this element vanishes gives the equation:

$$\left(\widehat{zz} + h\frac{\partial \widehat{zz}}{\partial z}\right)\sin\varphi'\left(r + \frac{dr}{2}\right)\theta dr = \widehat{rr}\cdot h\cdot r\cdot\theta - \left(\widehat{rr} + dr\frac{\partial \widehat{rr}}{\partial r}\right)(r + dr)h'\cdot\theta + \widehat{\theta\theta}\sin\theta\cdot h\cdot dr.$$

We have further:

$$h = R\varphi + R'[\cos\varphi' - \cos\varphi]$$
$$h' = R\varphi + R'[\cos(\varphi' + d\varphi') - \cos\varphi]$$

Expansion of this equation, keeping only terms of the lowest order, gives:

$$\widehat{zz}\frac{r^2}{a} = \widehat{rr}\left[\frac{3}{2}\frac{r^2}{a} - \frac{a}{2} - R\right] - r\frac{d\widehat{rr}}{dr}\left[R + \frac{1}{2}\frac{a^2 - r^2}{a}\right] + \widehat{\theta\theta}\left[R + \frac{1}{2}\frac{a^2 - r^2}{a}\right] \quad (19)$$

Into this equation involving the three stress components we may now substitute the particular relations given by our analysis above, namely, $\widehat{\theta\theta} = \widehat{rr}$, and $\widehat{zz} = \widehat{rr} + \widehat{zz}_a$. $\widehat{zz}_a$ is the flow stress at the external surface where the other two components of stress vanish, and is therefore the flow stress for an ordinary tension test at the particular elongation under homogeneous conditions. We replace the notation $\widehat{zz}_a$ by F, for flow stress. The equation (19) now becomes an equation for the single component $\widehat{rr}$:

$$\frac{d\widehat{rr}}{dr}\left[R + \frac{1}{2}\frac{a^2 - r^2}{a}\right] + \frac{r}{a}F = 0 \quad (20)$$

The variables are separated, and the equation may be at once

integrated, giving, together with the boundary condition, the closed solution:

$$\left.\begin{aligned} \widehat{rr} &= F \log \frac{a^2 + 2aR - r^2}{2aR} \\ \widehat{zz} &= F\left[1 + \log \frac{a^2 + 2aR - r^2}{2aR}\right] \end{aligned}\right\} \tag{21}$$

The connection with the load is given by:

$$\text{Load} = \int_0^a 2\pi r \widehat{zz} dr = \pi F(a^2 + 2aR) \log\left(1 + \frac{1}{2}\frac{a}{R}\right)$$

Also

$$\widehat{zz}_{aver} = \text{Load}/\pi a^2 = F\left(1 + 2\frac{R}{a}\right) \log\left(1 + \frac{1}{2}\frac{a}{R}\right) \tag{22}$$

The factor $\left(1 + 2\frac{R}{a}\right) \log\left(1 + \frac{1}{2}\frac{a}{R}\right)$ should be divided into $\widehat{zz}_{aver}$ in order to obtain $\widehat{zz}_a$ or F. $\widehat{zz}_{aver}$ has been used hitherto in constructing strain hardening curves or stress-strain curves. It is F or $\widehat{zz}_a$ which should properly be used for such curves, for this is the flow stress at the given strain under conditions such that the other two principal components of stress vanish. $\widehat{zz}_{aver}$ is often referred to as the "true stress." In view of the magnitude of the correction factor, this now appears to be an unfortunate and confusing nomenclature. It is always confusing to propose a revision of accepted nomenclature, but it is sometimes necessary. I propose the following as perhaps leading to a minimum of confusion. Call $\widehat{zz}_{aver}$ the "uncorrected true stress" and F or $\widehat{zz}_a$ the "corrected true stress."

By substituting the explicit expression for $\widehat{rr}$ into equation (16) it is possible by successive differentiations to obtain an explicit expression for $\partial^2 zz/\partial z^2$, but there seems no particular interest in writing this out.

The procedure in the last step of the solution, from page 569 on, was suggested by the method used by Siebel. The nature of the approximations made by Siebel was such that it is difficult to estimate the degree of approximation to be expected of his final solution. He solved the problem for two dimensions, in rectangular co-ordinates x and z, the y co-ordinate running to infinity and not entering the solution. The $Y_y$ component of stress was set equal to zero. Under these assumptions his solution was approximate because he effectively set the h and h′ of the analysis above equal to each other, this discarding a finite term, and he also effectively set $\widehat{zz}$ = const for a first integration. The resultant solution was

finally applied to the cylindrical case merely by substituting r for x in the formula and integrating around the circle, and without any consideration of the effect of the stress component $\widehat{\theta\theta}$ which must of necessity appear when passing to cylindrical co-ordinates. Siebel's final formula was:

$$\widehat{zz}_{aver} = F\left(1 + \frac{1}{4}\frac{a}{R}\right)$$

Siebel's formula for the hydrostatic tension on the axis is a less good approximation than his formula for $\widehat{zz}_{aver}$.

## DISCUSSION

**Written Discussion:** By R. W. Mebs, associate physicist in metallurgy, National Bureau of Standards, Washington, D. C.

Experimental evidence is far from convincing that the von Mises condition holds true for states of triaxial tension. It would require only a small deviation from von Mises assumption in order to cause an effective decrease in the flow stress at the center of the specimen.

The assumption that hardening is constant all the way across the neck, independent of hydrostatic tension, appears to be untenable. Micro-examination of polished specimens of fractured tensile bars, short distances removed from the fractures, reveals a decrease in strain hardening as one approaches the axis. The longitudinal stress-gradient across the specimen thus is largely replaced by a deformation gradient. The initiation of a "brittle", or better, "separation" fracture at the center of the specimen could be attributed, in part, to the smaller strain hardening at that point, as well as to greater hydrostatic tension.[4]

### Oral Discussion

M. GENSAMER:[5] This paper entered prominently into the cohesive strength symposium discussion Tuesday afternoon and perhaps it might be well to point out why it came into that discussion. There is a possibility that it could be used to help us in our understanding of what happens in notched bars. The elastic solution for notched bars tells us that the stresses are greatest at the root of the notch, that is, at the surface of the specimen. The plastic solution that Dr. Bridgman has given us tells us that the situation is just the reverse of this. The stresses are a maximum at the axis. When we test a notched bar, if it breaks without any elastic deformation, the stress is greatest on the outside. If it flows enough so that the deformation is uniform across the cross section as Dr. Bridgman has assumed, then we have the maximum stresses on the center line.

When the specimen deforms relatively little before it breaks so that the elastic stress distribution is not changed too much, we should have a combination of the two states of affairs; and it may be, as Dr. McAdam has contended,

[4] D. J. McAdam, Jr. and R. W. Mebs, "An Investigation of the Technical Cohesive Strength of Metals," American Institute of Mining and Metallurgical Engineers, Tech. Pub. No. 1615, *Metals Technology*, Aug. 1943.

[5] Professor of metallurgical engineering, Carnegie Institute of Technology, Pittsburgh.

that the stresses are not as nonuniformly distributed across the section of the specimen as we might think; certainly not as nonuniformly distributed as we would guess from the elastic solution. There is a fair chance that Dr. McAdam's conclusions and arguments based upon a relatively uniform stress distribution are not so bad.

I think Dr. Bridgman's contribution will not only enable us to correct stress-strain curves but it will help greatly in our understanding of the behavior of notched bars, which is a practical problem.

### Author's Reply

The discussion of Mr. Mebs opens the question of the validity of various approximations made in the solution. It must of course be recognized that various approximations were made; the question is how good were these approximations, and whether it is better to apply the correction for nonuniformity of stress deduced on the basis of the approximations or to neglect the correction.

With regard to the failure of the von Mises condition under triaxial stress it is to be remarked that fortunately this question need not be considered because the actual solution shows a biaxial stress (two of the principal components equal) all the way across the section, and the von Mises condition is as applicable here as it is in the situations from which it is derived.

With regard to the assumption that hydrostatic tension does not affect hardening, numerical data were given in the body of the paper that indicate that the effect must be small. It is difficult to know what quantitative weight to attach to Mr. Mebs' statement that micro-examination of fractured tensile bars shows a decrease in strain hardening toward the axis, since no numerical values were given nor was the method of measurement indicated. If the method was, as may be suspected, a micro-hardness method then it is to be considered that the parallelism is by no means close between hardness and "strain hardening", as some unpublished experiments of my own show.

The most important deviations from exactness in our solution doubtless arise from strain hardening. But strain hardening does not proceed at a rapid enough rate to be a very important factor in my opinion. This may be illustrated by a numerical example. Consider a representative steel which fractures at a natural strain of unity, at which the ratio $a/R$ also has approximately the value unity. For the tensile stress at fracture on the periphery of the neck we take a representative value 225,000 pounds per square inch. The analysis of the paper shows that under these conditions the tensile stress on the axis, derived on the assumption of uniform strain, is 1.4 times greater, or 315,000 p.s.i. Let us now suppose that the stress is uniform all the way across, the difference of stress between axis and periphery which would naturally arise from the curvature of the contour being compensated by an enhanced stress at the periphery due to greater strain there and the accompanying greater strain hardening. The strain hardening at the periphery must be sufficient to raise the stress from 225,000 to 315,000. Representative experimental values for the strain hardening of this steel indicate an increase of flow stress of 90,000 p.s.i. for an increase of strain of unity. This means that the natural strain at the periphery would have to be greater by unity than that at the center, or the elongation at the

periphery 2.7 times greater than that at the center. If one were to make a rough free-hand graphical construction of the lines of flow which might give rise to this large difference of strain, I think it will be plain that any such difference of strain between axis and periphery cannot be entertained. Although the mathematical problem has not been exactly solved I believe that on the basis of geometrical experiments like this one can convince oneself that the approximation is not a bad one and that it is much better to apply the correction than to neglect it.

With regard to notched bar experiments brought up by Dr. Gensamer the assumption of uniform strain is doubtless less applicable, but I believe that nevertheless the deviation of the stress from uniformity across the section at the notch must be qualitatively like that found above for necked bars and quantitatively probably exaggerated in comparison with values ordinarily attained in necked specimens because of the very large value of a/R. This it seems to me may have an important bearing on the interpretation of notched bar experiments.

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